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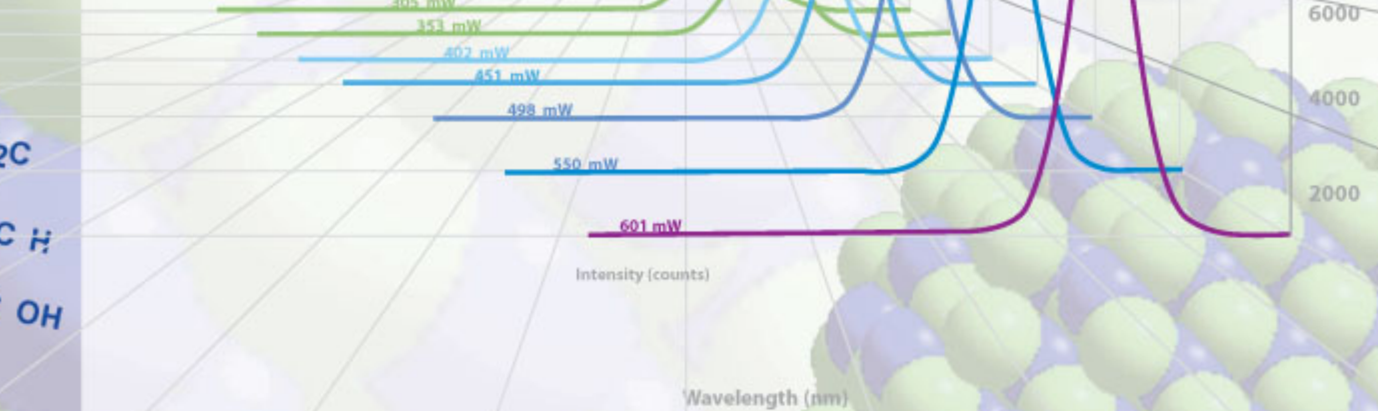
Office of Energy Efficiency & Renewable Energy

National Renewable Energy Laboratory

Director's Discretionary Research and Development Program

Annual Report Fiscal Year 2003



October 2003 NREL/MP-700-34845
Contract No. DE-AC36-99-GO10337

Director's Discretionary Research and Development Program

Annual Report Fiscal Year 2003

National Renewable Energy Laboratory

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Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
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Contract No. DE-AC36-98-GO 10337

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Introduction

The Director's Discretionary Research and Development (DDRD) program is designed to encourage technical innovation and build new research and development capabilities at the National Renewable Energy Laboratory (NREL). DOE-EE's (Office of Energy Efficiency and Renewable Energy) policy for the DDRD program enables NREL's Director to:

"…approve for funding, projects put forth by Laboratory staff which propose to explore and/or develop innovative or creative opportunities within mission areas assigned to the Laboratory. Projects should advance research and development directed toward solving present scientific or technical problems; or should be experiments and analysis directed toward determining the merit and utility of new ideas or concepts."

The DDRD program is critical for NREL' s long-term viability. It provides a means of incubating and maturing new concepts so that they can be introduced into the innovation pipeline (Figure 1). The new, early-stage concepts explored through the DDRD program provide a basis for proposing new technical directions to DOE. It not only serves as an incubator for testing new research concepts, but it also contributes to the knowledge base of the Laboratory. By enabling the pursuit of cutting-edge science, engineering and analysis, it enables researchers to stay at the forefront of discovery. This, in turn, enhances NREL's reputation and enables the laboratory to attract new talent and collaborators.

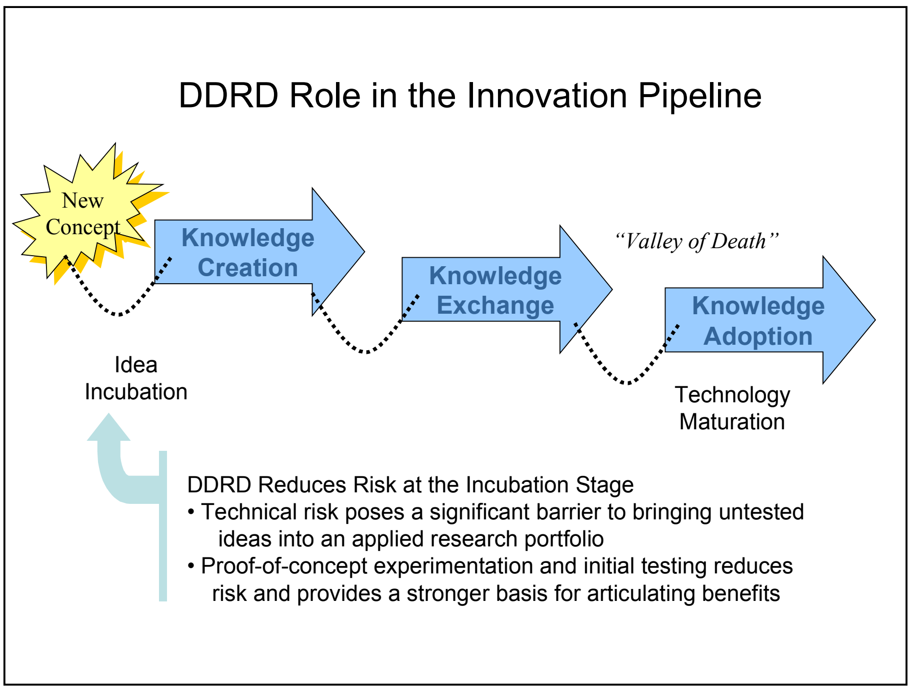


Figure 1. *NREL's DDRD Program enables new concepts to reach technology maturation.*

NREL's 26 DDRD projects active in fiscal year (FY) 2003 address a wide range of strategic research topics in advanced measurement and characterization, biological and chemical processing, biotechnology, materials and materials processing, and thermal and electrical systems (Figure 2) that cross-cut and have the potential to serve many technologies and programs. The projects test innovative concepts that can feed directly into current DOE-EE programs, such as solar energy or geothermal, or that support advancement of scientific knowledge through national focus areas, such as nanotechnology, that will provide the foundation for new technology innovation in the future.

The outcomes of these projects include scientific discovery and advances, creation of new or enhanced core competencies at NREL, as well as new or enhanced collaborations, publications, presentations, intellectual property, follow-on funding, and opportunities to explore new concepts that will lead to new technical development, or to enhancement or expansion of NREL's capabilities to carry out its mission. With this focus, the DDRD project scientists continuously revitalize the scientific and analytic stature of NREL to serve as a resource for DOE's missions.

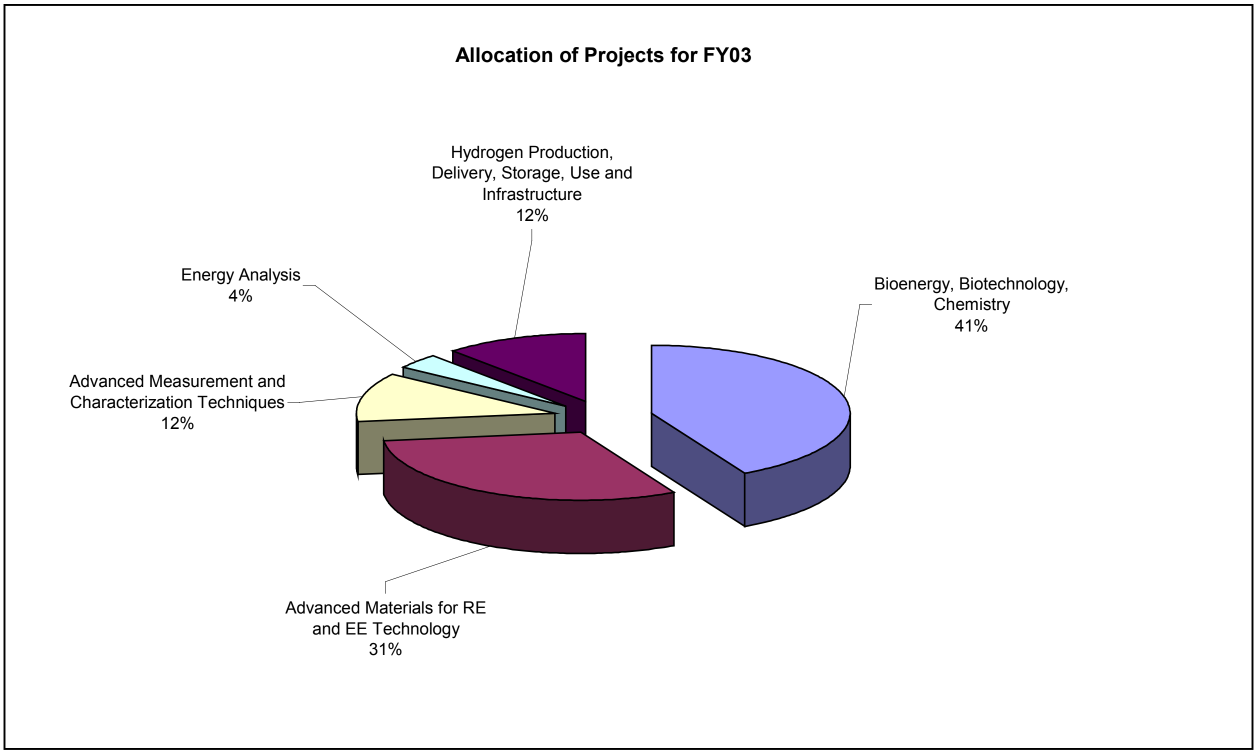


Figure 2. *NREL's 26 active DDRD projects address a wide range of strategic research topics and have the potential to serve many technologies and programs.*

Program Overview

DOE's Office of Energy Efficiency and Renewable Energy (EERE) established the DDRD program in December 1998, and NREL implemented it in early 1999. DOE-EE's policy for the DDRD program enables NREL's director to approve funding for projects put forth by staff to explore or develop innovative or creative opportunities within mission areas assigned to the Laboratory.

NREL's mission supports and reflects the DOE-EE mission, and is to develop renewable energy and energy efficiency technologies and practices, advance related science and engineering, and transfer knowledge and innovations to address the nation's energy and environmental goals. NREL strives to continue being a valuable resource for DOE and other sponsors in their search for solutions to the nation's global development needs and issues.

The Director's Discretionary Research and Development (DDRD) program provides NREL scientists with the opportunity to propose and pursue innovative, ideas for building new and enhanced capability at the laboratory. The program is internal in nature, it encourages and allows NREL scientists to stay at the forefront of their scientific fields.

As specified in NREL's policy, DDRD Program goals are as follows:

- Maintain the scientific and technical vitality of the Laboratory
- Enhance the Laboratory's long-term viability by strengthening existing core competencies and building new capabilities
- Enhance the Laboratory's ability to address future DOE missions
- Foster creativity and stimulate exploration at the forefront of science and technology
- Serve as a proving ground for new and potentially high-value mission-enhancing activities.

Over the past five fiscal years, over 40 projects have been funded through DDRD, ranging from small projects funded for less than $50K to large projects funded for $300K to $500K. These projects contributed to the long-term viability of the laboratory as a national and international resource and provided hundreds of NREL researchers with a creative environment within which they have been able to pursue innovative, cutting-edge ideas.

Through these projects, researchers have contributed to building new capabilities for NREL and to strengthening its core competencies in a variety of areas, including: fundamental renewable energy conversion science; renewable energy and energy efficiency technology development; renewable energy and energy efficiency systems, simulation, and modeling and integration; advanced measurements, characterization, and analytical techniques; and energy analysis and decision support.

The result has been continuous development of the Laboratory's technical core competencies (below), providing fundamental scientific innovations in renewable energy and energy efficiency programs (e.g., solar energy, wind energy, bioenergy, hydrogen, distributed generation, etc.) and providing timely responses to the nation's growing demand in these areas.

In addition to expanded capability, the outcomes of DDRD projects include scientific discovery and advances, new and enhanced collaborations, publications, presentations, intellectual property, follow-on funding, and very importantly – scientific leadership and domestic and international visibility for NREL. Many of the project outcomes bring new capabilities to more than one of the current DOE programs.

According to EE policy, the DDRD program may use up to 2% of the Laboratory's annual estimated funding from Appropriations, excluding funding specifically identified for capital equipment or for construction. The specific level of funding is negotiated annually between NREL and the DOE Golden Field Office (GO), in consultation with the EE Office of the Assistant Secretary. In FY 2003, the approved ceiling was $3 million. Individual projects can be funded up to $500,000 for a period of performance up to three years, subject to annual funding authorization.

This annual report lists funded and completed projects in FY 2003, describes each project and its outcomes, and summarizes the status and achievements of the DDRD program during FY 2003 with some examples of historical impacts. Of special note is the section on *Program Management,* which elucidates enhancements that NREL is making to strengthen the impact of the DDRD investment on the long-term viability of the Laboratory and the programs it benefits. The Appendices contain NREL and DOE DDRD policies, the DDRD Proposal Template, and acronyms and symbols.

These examples vividly demonstrate the value of the DDRD program, which places NREL and its researchers at the forefront of science and continuously enhances the viability and vitality of the Laboratory as a national resource addressing the energy needs of the future in a sustainable manner.

The successes of all scientific research, investigations and discoveries are made visible through presentations, technical seminars, poster sessions, publications, proposals, new collaborations, and intellectual property, as well as through success stories published on the NREL Intranet.

Based on NREL DDRD program goals specified in the policy, NREL's measures of success are:

- Significant impact on achieving Laboratory goals and mission, and on NREL's advancement in local and international scientific and business communities

- New or enhanced core competencies and IP creation that further NREL's mission (Records of Invention, Patents and Patent Applications, Licenses)
- Enhanced scientific and technical vitality and visibility (including scientific recognition, publications, proposals, presentations, awards and conferences)
- Expansion and improvement of Laboratory resources (facilities, staff, equipment, funding)
- New or enhanced collaborations (partnerships, sub-contracts, CRADAs, WFOs) that increase Laboratory's ability to address future DOE missions
- Stimulated innovation through:
    - Proposal teaming
    - Laboratory participation in proposals and projects
    - Laboratory participation in DDRD presentations and seminars.

Program Management

In the last year there were significant changes made to the process of soliciting and funding project proposals for the DDRD Program. To date, the Program has been very successful with scientific discovery, creation of knowledge and intellectual property, and building the technical capabilities of the Laboratory. The process improvements were directed at enhancing the outcome of DDRD investments and their alignment with NREL's overall strategy. Beginning in 2003, there are two means of submitting proposals:

1. The Principal Investigator submits a pre-proposal during the Annual Planning Process. Executive management decides whether to accept or reject the pre-proposal based on several factors including alignment with Laboratory priorities; potential of building needed capabilities enhancing NREL's long-term viability, and overall strategic merit. Once a pre-proposal concept is accepted, a formal DDRD project proposal is written and submitted to the process for technical review.

2. A Lab-wide Call is announced for investor-initiated DDRD Project. These proposals are intended to be discovery-oriented, pushing the front view of knowledge.

Proposals submitted via either method may be funded for up to $500K with a maximum duration of 3 fiscal years. All DDRD projects are subjected to an annual review where decisions are made to continue the project as planned, alter its course, or terminate the effort. These decisions are based on progress, findings, funding availability and continued relevancy of the effort.

Legacy of Program Success and FY03 Progress

This section of the report describes the legacy of DDRD program success over the last five years, including the most prominent scientific achievements that flowered from over 40 projects financed by the program during this time period. Some of the projects discussed in this section begun under the FIRST program and were continued under DDRD program after it was launched in 1999.

This section will also describe the current projects, new and enhanced ideas, and their development and progress during the FY03.

Advanced Materials for Energy Efficiency and Renewable Energy Technology

Successes in the past five years:

- In FY98-00 Kannan Ramanathan found a simple, inexpensive, polycrystalline material for use in thermophotovoltaic systems.

  NREL helped pioneer the technology for making low-band-gap thermophotovolatic (TPV) cells that convert infrared light, such as that generated by the heat of engines, into electricity. But the cells are expensive, single-crystal cells made with III-V materials, with a market limited to those who can afford them (such as the military).

  In an effort to design an advanced, inexpensive thermophotovoltaic cell, researchers investigated a promising polycrystalline material. Although their research showed that this material was inadequate for the proposed application, they were led to investigate an alternative material with better characteristics.

  Two new thin film materials for TPV applications were developed. They could serve as low band gap converters in a tandem solar cell. This research provides a foundation for further development of new TPV and PV devices.

  This work represents the first demonstrations of viability of thin-films for thermophotovoltaics, providing a technical foundation for a potential terrestrial, consumer application for the technology. It also provided possible low band-gap cells for high-performance multijunction polycrystalline cell technologies.

- In FY98-00 Suzanne Ferrere gained a better understanding of the dye sensitization process in solar cells, updated theories of molecular photoconversion, and established a foundation to obtain basic research funding.

  To achieve this result, Suzanne and other NREL scientists explored the use of iron-based dyes in photochemical cells. They found that structural and environmental changes have an impact on the sensitization ability of the complexes in dye-sensitized solar cell devices. They also determined that that iron sensitizers are viable alternatives to the more commonly used ruthenium-based analogues. Upon presenting these results to conferences and symposia, the researchers were invited to submit proposals to the Office of Basic Energy Sciences to obtain funding for basic research.

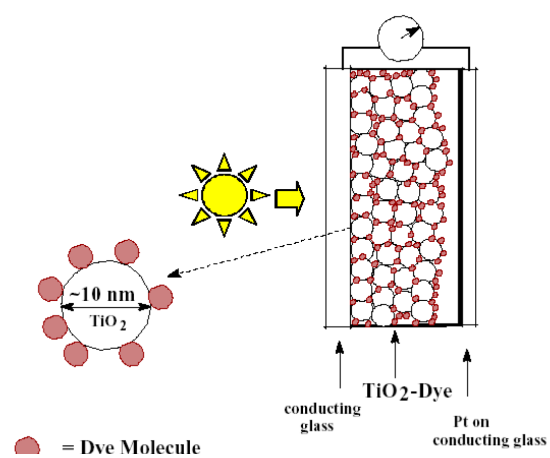


Figure 2*. In their work on dye-sensitized solar cells, Suzanne Ferrere, et al, found that iron-based dyes may be viable alternatives to more expensive rthenium based dyes that are currently used to absorb visible light and create charge carriers for the titanium based matrix of the cell.*

- A project conducted by Mark Hanna in FY99-00 resulted in improved conductivity of heavily doped III-V semiconductor layers and thus improved the efficiency of III-V multijunction solar cells and other devices.

  One of the problems in making very high efficiency multijunction cells from III-V materials is that normal doping techniques for the AlInP window layer used on such cells result in insufficient conductivity, which limits the efficiency of the entire device. Researchers investigated novel co-doping concepts to improve the conductivity of window layers used on multijunction solar cells — research that advanced the knowledge in materials science that is required for improving tandem solar cell performance. Researchers grew, co-doped, and characterized several important materials, with highly encouraging results. The codoping technique developed in this project may be used to produce heavily p-type doped AlInP layers with low atomic Zn diffusion as are required for tandem solar cells which are currently under development at NREL. This research advanced materials science knowledge necessary to improve tandem solar cell performance. The codoping technique is applicable to production of advanced optoelectronic devices such as high efficiency III-V solar cells and high-brightness LEDs.

- In FY99-01 Ted Ciszek investigated low-temperature processes for purifying metallurgical-grade (MG) silicon (Si) to the degree necessary for solar-grade feedstock, and collaborated with Sandia National Laboratories in experiments related to their LDRD on melt treatment purification of MG Si. Silicon is the PV material in about 85% of the ~300MW of modules sold per year. There is repeated concern by manufacturers about future supply of low-cost feedstock as the market grows by >30%/yr. In this project, groundwork for a promising new purification method was achieved and could be built upon. The promising approach shows remarkable reduction in metallic impurity levels, but much less reduction in levels of dopants such as boron and phosphorous. Additional work is required to incorporate purification steps for these dopants.

- In FY00 Harv Mahan investigated a new class of materials with potential application to the microelectronics and photovoltaic industries. Although the proof of concept was demonstrated, the researchers concluded that applications would be limited because of the characteristics of the films. However, their results led to the discovery of a hot-wire chemical vapor deposition a-Si:H alloy system with significant potential applications in the microelectronics industry.

- Research conducted by Angelo Mascarenhas and Mark Wanlass during FY00-01 made significant impact on one of NREL's strategic thrusts, distributed and hybrid generation, which is directed at the development and deployment of systems that produce both electrical and thermal power from a single source. Thermo photovoltaic (TPV) power generation systems, pioneered by NREL, represent a promising technology for combined heat and power. This project expanded on the existing experimental and theoretical knowledge base on nitrides developed at NREL. It also developed an improved materials approach for TPV converter fabrication, thus improving the efficiency of the TPV process and enhancing the likelihood of TPV system deployment, and achieved fundamental understanding of the behavior of nitrogen III-V semiconductors. The research uncovered an alternative approach and novel materials that will be used for making 3 and 4-junction solar cells and other electro-optic devices.

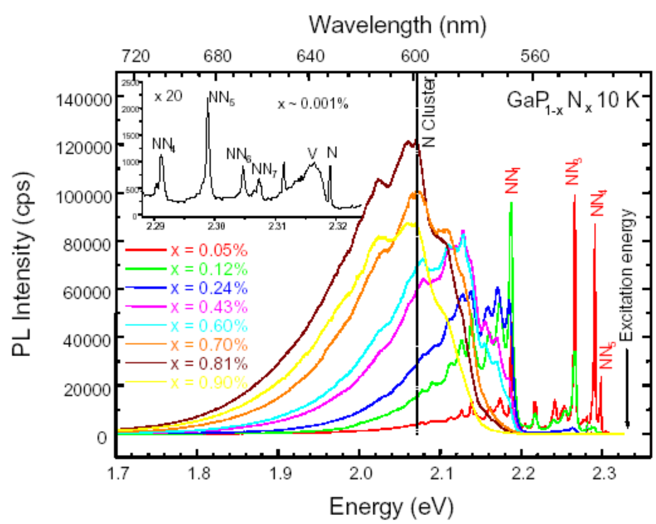
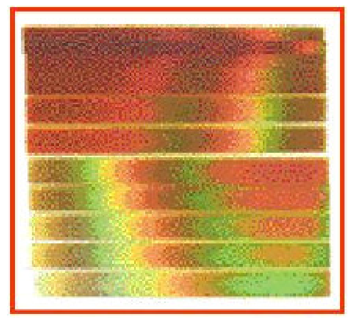


Figure 3. *In their project, Angelo Mascarenhas and Mark Wanlass explore the use of nitrogen to lower the band gap of III-V semiconductors in an effort to engineer materials that could be used to make efficient thermophotovoltaic devices. Here, photoluminescence studies help indicate the mechanism by which nitrogen doping reduces the band gap in III-V materials.*

- In FY00-01 Ted Ciszek successfully grew and characterized single crystals of Cd_2SnO_4, which is used in a thin film form as a transparent conducting oxide. Ted and other researchers explored several options to optimize thin-film transparent conducting oxides, which allow light into a thin-film cell and collect the current generated by it, thereby increasing efficiencies of polycrystalline

PV cells. The most promising approach appeared to be vapor transport growth in a high-pressure, high-temperature furnace; however, additional work is needed to achieve crystals suitable for characterization. Results pointed out the difficulty of large single crystal growth in this materials system.

- In FY00-01 Brian Gregg investigated dye-sensitized photochemical solar cells to gain a fundamental understanding of the dye-sensitization process and to use this understanding to develop a new class of sensitizing dyes. Dye sensitization emerged as an unexpected alternative to conventional methods of converting solar energy. The best dye-sensitized solar cells now reach an efficiency of around 10% and cost potentially much less than silicon or thin-film solar cells. Although we are beginning to understand dye cells, there are still a number of open questions. This research was aimed at developing a new understanding of fundamental aspects of dye-sensitization and at developing a new set of sensitizing dyes. Researchers made key discoveries with respect to dye adsorption, hole injection, and dye synthesis, and employed a new synthetic approach. They also discovered a way to dramatically increase the current efficiency of the new perylene dyes and of other dyes. This is a real breakthrough, and although the exact mechanism of the enhancement is still under study, researchers have clarified several contributing factors. This effect may be of major importance for both fundamental understanding of dye cells and for their practical applications. For the first time, scientists can tune the properties of the semiconductor to match the requirements of the dye; this provides a versatile analytical tool for characterizing dye cells and also enables the use of new classes of sensitizing dyes such as the perylene sensitizers. Researchers devoted the remainder of this project to the study and optimization of the numerous synthesized perylene dyes and to characterizing the important enhancement effect.



- Research conducted by David Ginley and John Perkins during FY00-02 resulted in NREL developing a solid-state combinatorial capability for the synthesis and discovery of new electronic materials as well as for the optimization of existing materials that can be used as photovoltaic absorber layers, transparent conductors, and intercalation materials for lithium batteries. Researchers also proposed a novel combinatorial approach, aimed specifically toward solid-state electronic materials for renewable energy applications that could accelerate the process of discovery by factors greater than 100.

  The work developed deposition and analysis systems needed to facilitate combinatorial solid-state discovery and an array of combinatorial tools, and performed a set of initial experiments to demonstrate the utility of the approach. It was demonstrated that the combinatorial method can significantly reduce the time it takes to explore, develop, and optimize new or existing optoelectronic materials of interest. The combinatorial tools developed by NREL researchers are being applied in an expanding role in the National Center for Photovoltaics.

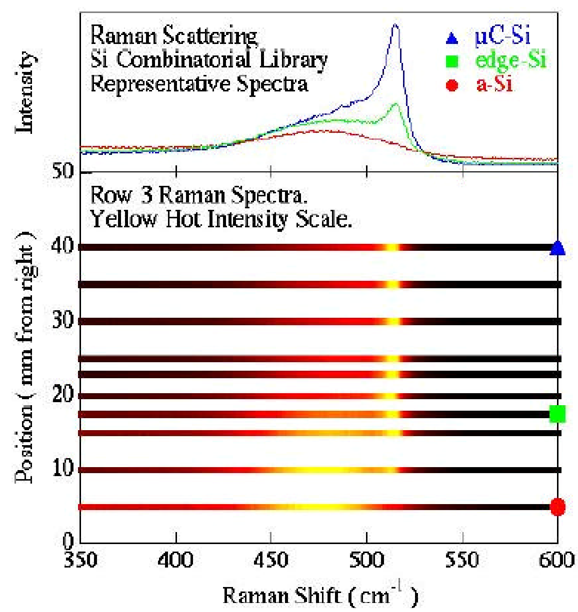


Figure 4. *David Ginley and John Perkins developed a combinatorial capability to synthesize and discover new electronic materials and to optimize existing materials. Here, they show a 10-row combinatorial silicon library deposited by hot-wire CVD (top, and an analysis of one of those rows using Raman scattering.*

- In FY00-02 Ping Liu applied a new materials-synthesis approach developed at NREL to metal oxides that are of great interest to industry in improving the performance of lithium batteries, electrochromic, and chemochromic devices. This, in turn, will have a direct impact on the battery, electrochromic, and sensor industries. In the past two decades, research on ion-insertion metal oxides has established that one of the limitations for lithium batteries and electrochromic devices is governed by the diffusion of Li+ or H+ in the oxide framework.

  Employing a highly porous material is one of the strategies used to reduce the length of the diffusion path and increase the performance. This research is directed at solving the dilemma of performance versus manufacturability. High-performance materials are often difficult and expensive to manufacture. The synthesis approach proposed in this research should provide high-performance materials that can be inexpensively manufactured. In this project scientists applied an NREL-pioneered approach to synthesize several mesoporous metal oxides – vanadium oxide, tungsten oxide, manganese oxide, and nickel oxide – that are of great interest to industry for improving the performance of lithium batteries, electrochromic, and chemochromic devices. In particular, the researchers developed an innovative approach to prepare manganese oxide at room temperatures. This manganese oxide has a unique nanocrystalline/mesoporous structure that gives it outstanding kinetics and cycling capability as a lithium battery cathode.

- Research conducted by Mowafak Al-Jassim during FY01-02 reduced the defect density in highly-mismatched, low-band-gap arsenide and phosphide semiconductors, and thereby developed a material with good minority-carrier properties as required for the next generation of high efficiency multijunction solar cells and thermophotovoltaic devices. Researchers explored and developed a novel approach to highly mismatched epitaxy that is likely to result in mismatched structures with greatly reduced structural defect densities, which, in turn, should allow a more flexible approach to designing multijunction solar cells and other minority carrier devices, such as LEDs and laser diodes. To date, researchers have designed and fabricated a number of masks, and have used lateral epitaxial overgrowth (LEO) to make wafers with III-V films of low-defect density. They are now ready to use these wafers to fabricate entire cells.

- In FY02 Se-Hee Lee used an electrochemical supercapacitor to achieve reversible optical transmittance modulation in thin-films of transition metal oxides, a totally different approach from the current ion-insertion research in electrochromics. In the summer, about 10%-15% of electrical energy consumption in the United States is used for cooling buildings with air-conditioning systems, at a cost of approximately $10 billion per year. This project was aimed at improving energy efficiency by means of reducing the air-conditioning costs through the use of technology that quickly and reversibly changes the transmittance of coated windows to block the heat of the sun. The principle of this technology is based on a novel concept of electrochromism induced by supercapacitor discharge/charge. This type of electrochromism has advantages compared to current electrochromic technologies; i.e., the durability of electrochromic devices can be significantly improved, and the response time can be extremely fast. This is an innovative approach that could place NREL at the forefront of the field of electrochromics. Researchers discovered an excellent material – amorphous ruthenium oxide – and developed a method to deposit this material on indium tin oxide coated glass, and showed that it had excellent properties as a supercapacitor and electrochromism. In fact, this material will quickly and reversibly modulate optical transmittance by 50% over the entire visible spectrum, making it an excellent candidate for electrochromic coatings. Using this material, the researchers also invented a reliable method for sensing the presence of hydrogen, which could prove to be very important for safety concerns with the storage and use of hydrogen.

2003 Developments:

- The project conducted by Steve Smith and Garry Rumbles aims to use the fluorescence of single molecules as an ultra-sensitive probe of exciton energetics and dynamics in conjugated polymers and organic-inorganic composite particles. Using the spatial, temporal and statistical properties of single-molecule fluorescence events, information regarding structure, dynamics and chemical environment of the fluorophore can be gathered. This information will be invaluable in understanding the operation and limitations of current and future polymer-based opto-electronic devices. In the first six months of this project, human resources and equipment were secured and collaboration was established with the Bio-Energy Center to pursue common interests in single-molecule detection and imaging.

- Se-Hee Lee's research intends to develop unique nano-composite materials of transition metal oxides for solid-state supercapacitor applications and to study their electrochemical characteristics. The aim is to develop a new class of solid-state supercapacitors based on the novel nano-composite structure. This research places NREL at the forefront of solid-state science and technology in the field of energy storage. In FY03, thin films of Ni-Ta oxide nano-composites were generated and their electrochemical behavior was examined. The researchers created a unique nano-composite mixture (of poly crystalline nano-particles of nickel oxide intimately surrounding an amorphous tantalum oxide electrolyte), which constitutes an ideal structure with great potential for fabricating improved solid-state supercapacitors.

- Shaun Shaheen conducted fundamental research on organic semiconductors and organic / inorganic hybrid nanostructured materials with the end goal application of low cost, high efficiency solid state indoor lighting from organic white light emitting diodes (OWLEDs). This program will make significant contributions to the basic science underlying organic semiconductor devices and organic-based solid-state lighting. This includes topics such as material design and development, fundamental understanding of the charge transport, luminescence and photophysics in these materials, and device design, fabrication, and integration.

  In FY03, the team investigated transport in conjugated (electronically active) polymer films, demonstrating the effect of thermal annealing of the films on the charge carrier mobility. The researchers successfully made composite materials consisting of mesoporous nanostructures of TiO2 intercalated with conjugated polymer. These composites show good filling of the porous TiO2 structure with the polymer, a promising first step toward making devices from these materials. The team also grew a 'carpet' of nanostructured ZnO nanofibers, a promising structure for device applications utilizing the high electron mobility of ZnO nanofibers. The team has begun making polymer/ZnO nanofiber composites with promising initial results.

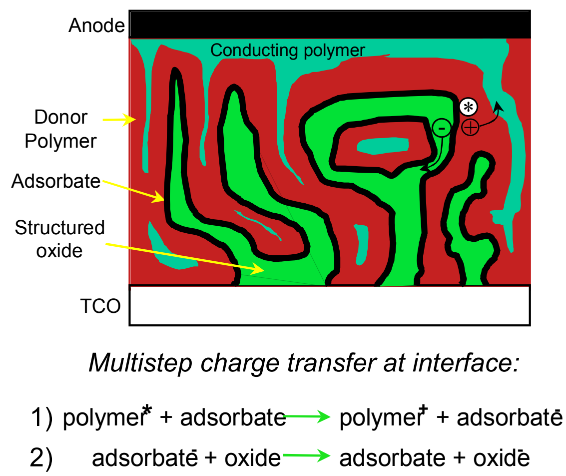


Figure 5. *Two-dimensional slice of basic concept of organic PV device. The donor polymer absorbs light to produce excitons (charge carriers of bound electron and holes). The electrons are siphoned off by an adsorbate, and transported via the structured ZnO nanorods to be collected by the TCO. The holes are siphoned into the hole-conducting polymer, which transports them to the anode.*

  An important aspect of nanostructured composite material is the interface between the oxide and the polymers, which affects the electron transfer rate between the two materials. The team has shown that charge transfer characteristics of the interface can be improved by attaching molecular binding groups (surface adsorbates) to the oxide prior to introducing polymer into the structure.

  In order to optimize polymer device development, the team has worked on measuring the dialectric constant of the relevant optical layers for these devices, and on modeling the optical processes that occur during light generation. They have begun preliminary investigations into the optical properties of nanostructured oxide/polymer composite materials, with the aim of designing structures that yield enhanced forward light output.

A crucial factor in developing organic semiconductors is the capability to design and synthesize new organic molecules and polymers, and to choose among an infinite number of candidate molecules. In contrast, conventional semiconductors involve a limited palette of options to choose from. The team has begun preliminary computational studies of the relationship between the structure of organic molecules/polymers and their electric/optical properties.

- Thermoelectric solid-state energy conversion devices for cooling and power generation currently use bulk semiconductor alloys as the thermoelectric material. NREL researcher Mark Hanna attempted to fabricate and characterize nanostructured III-V thin films based on quantum dot superlattices (QD-SL), which are expected to have a greatly improved thermoelectric performance over their bulk constituents. This work should lead to several scientific publications and form the basis for a new materials science research area at NREL. In FY03, this project designed and laid out a photolithography mask set for the fabrication of the device structures that will be used to measure cross-plane thermal conductivity, Seebeck coefficient, and electrical conductivity of the quantum dot superlattices. The team performed calibration growth runs of InGaAs SK islands and Se-doped GaAs to determine suitable conditions for forming a high density of InGaAs islands and to determine n-type doping behavior. Finally, the team obtained necessary equipment and began developing the program for controlling the experiment and collecting data.

- Jao van de Lagamaat introduced a unique approach that combines three interrelated diagnostic techniques (low-temperature and ambient tunneling spectroscopy, photocurrent transient spectroscopy, and electrochemical transistor setup) for characterizing the energy levels of individual quantized semiconductor nanoparticles and the dynamics of interparticle charge transport in assemblies of these nanoparticles. The combination of these techniques is expected to yield insight into the interplay between the energy structure of a single particle and interparticle transport. The research also involves the synthesis and characterization of dispersed nanoparticles and their assemblage as monolayers and multilayers. In FY03, the team rescoped the project to focus on quantized semiconductor nanoparticles, and found sources for the particles and required equipment. The researchers also raised the visibility of the project at an international conference and initiated international collaboration.

- Mowafak Al-Jassim focused on development of the novel approaches to the epitaxial growth of highly mismatched semiconductor systems. Epitaxially grown, multijunction solar cells have been demonstrated at NREL and in Japan with efficiencies exceeding 30%. However, such cells are based on the lattice-matched multilayer structure of GaAs/GaInP. Furthermore, these cells and other high-efficiency devices (for example GaAs/GaAlAs and InP/GaInAs) are grown on expensive substrates such as GaAs and InP. The further development of such high-efficiency cells requires the incorporation of additional junctions using materials with appropriate band gaps; and, further reduction in cost will require deposition on less expensive substrates such as Si. Both of these requirements will probably involve mismatched epitaxial growth. In this project, researchers propose to explore and develop a novel approach to highly mismatched epitaxy. They believe this approach will result in mismatched structures with greatly reduced structural defect densities. This, in turn, should allow a more flexible approach to designing multijunction solar cells and other minority carrier devices, such as LEDs and laser diodes. In FY03, the team developed special templates and procedures for the growth of mismatched III-V layers, and increased the visibility of NREL's effort through two published papers.

- Anne Dillon, Jeff Alleman, and Harv Mahan investigated carbon single-wall nanotubes (SWNTs) that have a variety of unique electronic, optical, and mechanical properties making them promising candidates for a wide scope of applications including gas storage and separations, fuel cell membranes, batteries, photovoltaics, composite materials, nanoscale wires, and interconnects. However, for any of these applications to be ultimately realized, it is essential to develop an economical and scalable synthesis technique for the production of defect-free SWNTs at high yield, which may be easily purified. Such a method is not currently available. NREL researchers have demonstrated a "proof of concept" for a hot-wire technique for the production of

SWNTs. The researchers have high expectations for the optimization of this novel technique since it is a continuous rather than a batch process, utilizes a gas phase catalyst and should be economically scalable. In FY03, the team began assembly of the required equipment, applied for a patent on hot –wire production of SWNTs, and explored optimal catalyst incorporation methods, optimal synthesis temperatures, pressures and gas flow conditions. A number of papers are in preparation or have been submitted.

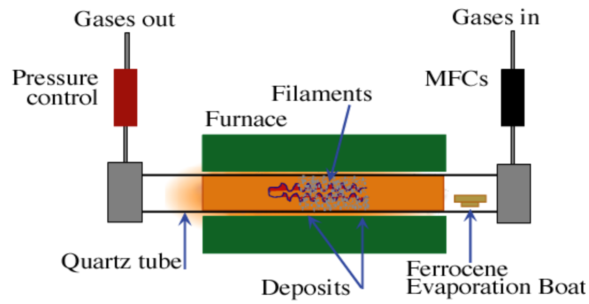


Figure 6. *Schematic of the hot-wire chemical vapor deposition (HW-CVD) system used by researchers Anne Dillon, et al to make single-wall nanotubes (SWNTs). This approach to making SWNTs is a continuous process system (as opposed to batch process) that has a great potential to reduce production costs while improving the purity of the nanotubes.*

Advanced Measurement and Characterization Techniques

Successes in the past five years:

- In FY98-00 George Radziszewski studied the role of organic radicals in oxidizing hydrocarbons, whether in combustion of renewable fuels or in the environmental processing of pollutants in the atmosphere, using cryogenic spectroscopy techniques.

  It would certainly be easier to understand a key chemical reaction if it took days to occur instead of its natural nanoseconds. To achieve this, researchers used near absolute zero temperatures to slow down reactions and isolate otherwise extremely short-lived organic radicals (hydrocarbon molecules with a hydrogen atom stripped off) that occur as a result of hydrocarbon combustion. This enabled them to use refined optical spectroscopy to “fingerprint” the radicals. They have published a paper conclusively showing success in fingerprinting radicals — something that has not been achieved in 30 years of attempts by others.

  The research has two direct benefits to businesses involved in combustion and atmospheric chemistry: (1) it leads to a detailed understanding of important chemistry in these processes, and (2) it provides spectroscopic signatures for analytical chemists dealing with these important radical intermediates.

  For NREL, researchers have developed a low-temperature photochemistry and spectroscopy technique that allows them to slow down the chemical reactions of organic radicals (which normally occur on the order of nanoseconds) and study the role that the radicals play in oxidizing hydrocarbons. This is a capability unique to NREL and is important for investigating fuel combustion and the environmental processes of pollutants in the atmosphere. The researchers have already used their technique to study the phenyl radical in detail and establish its basic electronic and vibrational spectroscopic signatures.

  The new spectroscopic analytical techniques establish NREL's leadership in this important area of basic science. It will also lead to a better understanding of combustion of renewable fuels, which could help increase combustion efficiencies and mitigate emissions of pollutants.

- In FY98-00 Steve Smith and Angelo Mascarenhas combined microspectroscopy techniques with NREL’s state-of-the-art ultrafast spectroscopy capabilities to perform high spatial and temporal resolution studies of thin-film photovoltaic materials.

In the important emerging class of polycrystalline PV materials, chemical composition, doping, and optoelectronic properties vary from grain to grain. With this project, researchers combined ultrafast spectroscopy with near-field scanning optical microscopy to develop an ultramodern technique for examining optoelectronic properties on the nanoscale, and correlating those properties to the material's sub-micron topography. This gives NREL unique capabilities for characterizing PV materials and greatly enhances its leadership in this field.

A low-temperature Near-field Microscope was developed and used to perform low-temperature spectroscopy of single and polycrystalline materials with a demonstrated resolution of ~200 nm. A scanning Solid Immersion Lens Microscope was developed and demonstrated to achieve ~0.5 um spatial resolution at cryogenic temperatures, and Optical Parametric Oscillator was developed to provide a tunable high-repetition-rate femtosecond pulsed laser source.

These powerful tools positioned NREL to undertake fundamental studies of individual grain boundaries. Developing these techniques, which aids in the understanding and elucidation of the effects of sub-micron structure on opto-electronic properties of PV materials is of pivotal importance to the engineering of more efficient, more economical polycrystalline solar cells.

- Research conducted by Bob Meglen during FY99-01 emphasized that timber companies currently have limited knowledge of the quality of standing timber, which hinders their ability to anticipate the economic resource and to direct various portions of the harvest to maximal use. NREL near-infrared (NIR) spectroscopy technology will allow them to drill a very small hole in the tree, insert an instrument probe, and know instantly key wood-quality parameters of the tree. Previous NREL work provided chemical analysis capability to determine if the tree had enough cellulose for making paper. This project added mechanical analysis capability to determine whether the wood will be strong and stiff enough to use for veneer or lumber.

Figure 7. *Researcher Bob Meglen uses his a probe, near infrared spectroscopy, and an algorithm on his laptop computer to determine mechanical properties of standing timber. This DDRD project resulted in an R&D 100 Award-winning technology.*

  The techniques have the potential to reduce energy consumption and gaseous emissions by direct improvement of biomass processing technologies, and improve the sustainability of an industry dependent on biomass. This research developed expertise for utilization of NIR for characterization of biomass; expertise being used in a number of new DDRD projects, and several WFO projects.

- In FY00-01 Brent Nelson advanced materials science by characterizing the bonding configurations in hydrogenated silicon thin-film (TF-SiH). This research involved a creative approach, at the forefront of materials characterization science to gain novel insights into the structural and electronic properties of TF-SiH materials. With this project as a proving ground, NREL researchers strengthened the characterization methodology for TF-SiH, which may be relevant to other thin-film semiconductors materials. They installed a new contact FTIR-ATR microprobe (a Fourier transform infrared spectroscope with an attenuated total reflection crystal) and used it to quantify the source of observed anisotropy in hydrogenated amorphous silicon. This new instrument extended NREL's capabilities in FTIR characterization and added to the core capabilities of thin-film silicon materials measurement and characterization for photovoltaics. The new contact FTIR-ATR microprobe allows for FTIR measurements on "real-life" substrates such as stainless steel, TCO coated glass, and other metal foils (traditional techniques require film growth on crystalline substrates - not used for actual applications). The FTIR techniques are useful for qualitatively determining crystalline inclusions within thin-film silicon. The ATR technique is exceedingly sensitive to oxygen impurities, which are below the detection limit of traditional FTIR techniques. Researchers discovered technique limitations and determined a low probability of using this technique for proposed use.

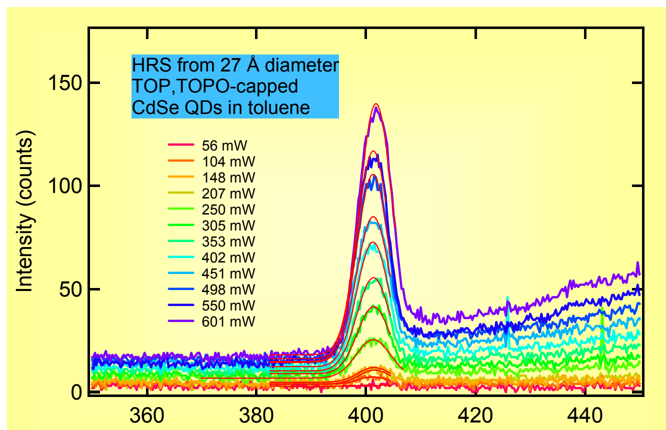


Figure 8. *Randy Ellingson used his experimental Hyper-Raleigh Scattering(HRS) setup (top) to produce an HRS spectra for a 27 Å-diameter CdSe quantum dot in toluene.*

- In FY00-02 Randy Ellingson developed a surface-specific second-order nonlinear optical spectroscopy technique. Surface reactions play a central role in photoelectrochemical, photocatalytic, and electrocatalytic reactions. Researchers developed a spectroscopy technique to study the second-order, non-linear surface reactions. This technique could provide insight into the surface chemistry of fuel-cell catalysis, dye-sensitization, and electron transfer, and may lead to improved designs for electrochemical and photoelectrochemical energy conversion devices. Researchers are establishing the capability to acquire surface second harmonic generation data and fit the results to theory. They successfully designed, constructed, and utilized a measurement system capable of sensitive measurement of the hyper-Rayleigh scattering intensity from liquid samples of colloidal quantum dots. Hyper-Rayleigh scattering provides information regarding the nonlinear polarizability of solvent and solute molecules, as well as colloidal particles such as nanocrystalline semiconductor quantum dots in solution samples. The results provide NREL with a new measurement technique with application to studies of nanomaterials in liquid suspensions. Since many approaches to using nanomaterials for solar energy conversion rely on self-assembly, any additional means of studying these colloidal nanomaterials are important. As we develop new ways to convert photoenergy into chemical and electrical energy, we'll have to be able to characterize charge separation and transfer processes. These processes can in principle be studied through energy- and time-dependent hyper-Rayleigh scattering.

- In FY02 Don Selmarten determined the merit of a newly proposed approach — single dot spectroscopy — for solving the existing problem of inhomogeneous spectral broadening in colloidal dispersions of semiconductor quantum dots, leading to new insight into the science of quantum confined semiconductor particles. The study of a single quantum dot could permit direct analysis of several important current topics, such as surface localization of charge on a single dot. These studies could bring about an unprecedented level of understanding of semiconductor energetics, leading to future research. The more complete insight into semiconductor fundamentals will subsequently result in higher efficiencies for PV systems. Additionally, a more comprehensive understanding of the underlying principles of quantum confined semiconductor science will make it possible to achieve a quantum dot solar cell. The researchers explored a novel technique to enable a precise experimental interrogation of distinct quantum confined semiconductor systems. They devised a unique method by which they could isolate single quantum dots for study. At project's end, however, the technique was not yet robust enough to allow spectroscopic characterization to proceed under all desired conditions.

2003 Developments:

- X-ray diffraction is the primary technique used to ascertain crystalline structure in materials, and thus it is a fundamental analytical tool. In this project in 2003, researcher Phil Parilla is establishing the capability at NREL to measure and analyze X-ray diffraction of single crystals. By establishing a set-up and core competencies in single-crystal X-ray diffraction, and analysis of data, this project will enhance NREL's ability to investigate and understand new material systems as they apply toward scientific and technological questions. In FY03, the team assembled required equipment and developed skills and knowledge of x-ray diffraction.

- The results of Ed Wolfrum's 2003 project directly support NREL's mission to develop energy efficiency technologies and practices with respect to building technologies. Energy usage patterns in buildings can influence indoor air quality, although the effects are often indirect and difficult to quantify. As the building envelope is made more impervious to heat loss (or gain) there are tradeoffs in the amount of fresh makeup air required to maintain air quality and the energy required to condition the outside air that is introduced. The work we have completed is an important first step toward establishing a significant NREL capability for the comprehensive understanding of trace organic compounds in building workspaces. In FY03, the project developed methods and techniques for unattended air sampling of building spaces and rapid interpretation of results. The team constructed automated air sampling units, collected ambient air samples from different building spaces at NREL, and performed chemometric analysis of the samples to identify chemical "fingerprints" of the different building spaces.

- Research on semiconductor nanoparticles conducted by Art Frank in 2003 has the potential to significantly impact energy efficiency, storage, and production. The fundamental knowledge gained from the study of the electronic properties of nanoparticles and arrays of nanoparticles will serve future nanoparticle-based technologies aimed at environmental and energy issues, where such considerations are important (e.g., quantum dot arrays, metals, photochromic and electrochromic displays, batteries, and catalytic systems). Moreover, future publication of the results in a peer-reviewed scientific journal will highlight NREL's position in the nanoscience area. The FY03 results demonstrated the feasibility of preparing organized monolayer assemblages of monodispersed ultrasmall TiO_2 nanoparticles and of studying them by techniques that are sensitive to probing the electronic structure of a single nanoparticle. The capability to organize nanoparticles in two- and three-dimensional structures is a major goal in nanoscience in general and in nanoparticle-based solar cells in particular. The team also submitted two proposals for further work.

Bioenergy, Biotechnology, Chemistry

Successes in the past five years:

- In FY98-00 Dan Blake investigated using sunlight and photochemistry to convert biomass into high-density fuels for use in internal combustion engines. High-density fuels are hydrocarbons that have additional energy due to the presence of 3-, 4-, or 5-membered rings. The formation of rings employing photochemistry may also be used to soak up and store sunlight energy. Success would position NREL at the forefront of this novel area of research and build NREL's capabilities in organic synthesis and photochemistry that can be applied in the Bioenergy initiative.

  The proof of concept was established – the scientists completed the synthesis and chemical and physical characterization of one of the target compounds, which has a significant increase in energy content and a slightly higher density. Two candidate compounds that have very high strain energy were identified. Photochemical conversion of natural products to higher energy density substances was achieved. Energy differences between precursors and strained ring compounds can be estimated with good accuracy using *ab initio* methods. Compounds with the highest predicted strain energy could not be synthesized.

The results demonstrate that compounds derived from biomass can be converted using photochemical means to products increased energy density. This can be applied to production of fuels or fuel additives and to store solar energy.

- In FY99-00 Ed Wolfrum attempted to: (1) control the yield and chemical composition of the poly-3-hydroxyalkanoate (PHA) polymers by controlling the growth conditions of the photosynthetic bacteria, and (2) increase understanding of the dynamics and efficiencies of photobioreactors for growth of microbial polymers.

  In this project, NREL researchers investigated a special class of photosynthetic bacteria (already isolated by NREL scientists) to produce *biodegradable* plastics. These microbes feed on dilute organic waste streams, storing energy as biodegradable plastics — similar to how animals store fat. In the first phase of this project, researchers manipulated growth conditions of the photosynthetic bacteria to control the yield and composition of the plastics.

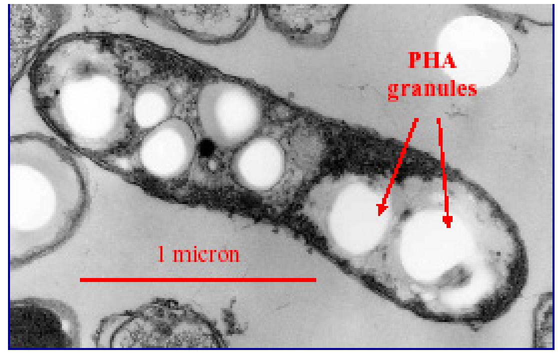


Figure 9. *Electron micrograph of the photosynthetic bacterium R. gelatinosus CBS. The PHA granules for producing biodegradable plastics are clearly visible.*

  NREL researchers successfully demonstrated the ability of several photosynthetic bacterial strains to operate in both light and dark. However, because the strains that produce well in the light are different from those that produce well in the dark, the researchers will continue to search for a single strain with high activities in both the light and dark, while considering a mixed-culture of bacteria to achieve the overall goal.

- The strategic thrust of Steve Thomas's project in FY99-00 was to establish a strong plant biotechnology research and development capability to better position NREL for its important role in bioenergy/biotechnology research and in development of national bioenergy initiatives. This project focused on development of reliable, high-throughput techniques that can be used to detect and quantify genetically determined chemical differences in plant biomass. The research crosscut two research centers at NREL and built capability to address multiple technology goals. This project demonstrated the utility of near infrared (NIR) and pyrolysis molecular beam mass spechometry (pyMBMS) as useful genetic screening tools and identified genetic variants harboring tagged genes that will be useful in future genetic engineering approaches to tuning biomass composition for conversion processes — a capability that holds great interest for industry. The researchers formed collaborations with industry and academic institutions, and were invited to join two projects of the National Science Foundation's Plant Genome Initiative.

- In FY99-01 Luc Moens' team proved that ionic liquids — salt-like compounds that occur as liquids at room temperature — can be used to convert biomass-derived carbohydrates, such as glucose and xylose, into useful chemicals. In the process, researchers learned how to prepare several types of ionic solvents on a routine basis; developed a procedure that allows products to be isolated and purified after completion of the chemical reactions; discovered a new reaction that may be of great use in lignin chemistry; and created new opportunities to affect chemical reactions without the use of environmentally unfriendly acids such as sulfuric acid — a significant step towards the development of new "green chemistry." In addition to developing the ability to synthesize a variety of ionic liquids that can be used for synthetic chemistry in biomass-related R&D, the scientists also developed new fluids for heat transfer and thermal storage, which can be used for the conversion of solar heat to electricity.

- In FY99-01 Dan DuBois gained an increased understanding of how to approach the cleavage of H-H and C-H bonds in catalytic processes.

  Nickel catalysts for hydrogen oxidation could lead to hydrogen fuel cells in which expensive platinum catalysts are replaced by much less expensive nickel compounds. Similarly, catalysts capable of activating the C-H bonds of hydrocarbons could lead to the development of low-temperature fuel cells that are capable of directly oxidizing hydrocarbons at the anode of the fuel cell without the need to first reform the hydrocarbon to produce hydrogen. However, many efforts to replace platinum in hydrogen fuel cells with cheaper catalysts have been unsuccessful, and no good catalysts exist, expensive or otherwise, for the low-temperature oxidation of hydrocarbons. Ultimately, this failure can be traced to the fact that our understanding of catalytic processes in incomplete, especially our knowledge of how to cleave H-H bonds and C-H bonds.

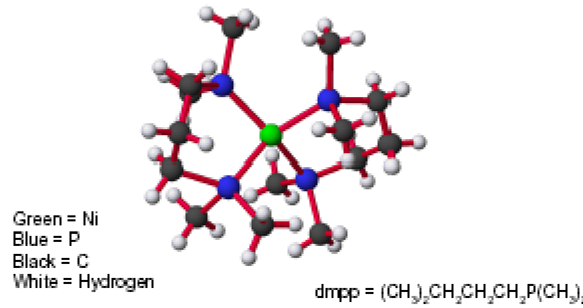


Figure 10. Molecular Structure of a nickel catalyst $[Ni(dmpp)_2]^{2+}$, a molecule capable of activating hydrogen and a candidate to replace relatively rare and more expensive platinum catalysts.

  Researchers designed, synthesized, and characterized new complexes that activate H-H bonds and catalyze the electrochemical oxidation of hydrogen. They demonstrated that the new complexes are thermodynamically favored over platinum complexes for heterolytic cleavage of C-H bonds. The hydrogen oxidation catalysts designed are not yet sufficiently developed to compete with well-studied platinum electrodes, but the researchers have advanced the fundamental science toward this goal.

  Fundamental research demonstrated that hydrogen oxidation based on discrete Ni complexes are feasible (as opposed to heterogeneous platinum catalysts) and suggest future research may result in practical Ni-based hydrogen oxidation catalysts. Better and cheaper hydrogen oxidation catalysts could result in cheaper hydrogen fuel cells based on a much more abundant metal (Ni as opposed to Pt).

- In FY99-02 Mike Seibert advanced scientific knowledge of photosynthesis by helping to define the assembly process and structural organization of the water-oxidizing system in the photosynthetic membranes of algae. This work may unlock some of the secrets of photosynthesis in the process, and it could help improve biomass production, algal hydrogen production, and artificial photosynthetic processes.

  Oxidation of water is not nearly as well understood at the molecular level as other aspects of photosynthesis. NREL scientists have developed strong expertise in isolating and examining the site of this reaction, a manganese-binding protein. Russian scientists have observed that this protein can also bind iron, probably at the manganese site. This project initiated collaboration with

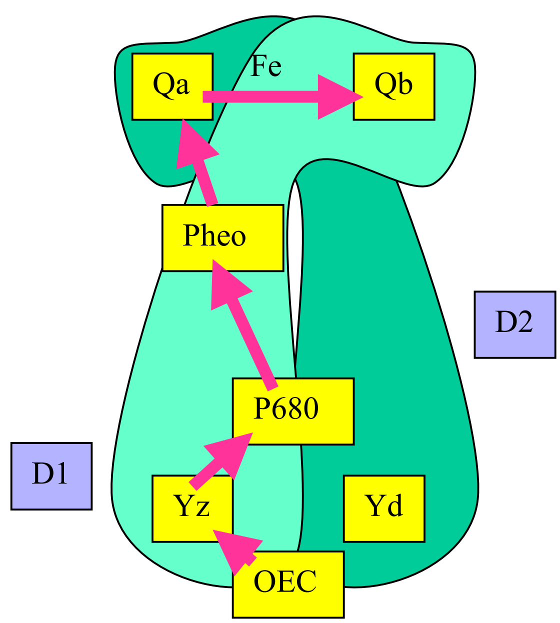


Figure 11. Mike Seibert, et al studied the water-oxidizing system of photosynthesis II (PSII), to try to enhance algal hydrogen production. PSII, which extracts electrons from water and releases molecular oxygen to the atmosphere, is a multisubunit membrane formed by two polypeptides, D1 and D2. The polypeptides bind all electron transfer components, including the oxygen-evolving complex (OEC).

the Russian team to study the effects resulting from substituting iron for manganese and the influence of certain arginine amino acid residues on the function of the Mn-binding protein complex.

In collaboration with two visiting Russian scientists, NREL researchers are well on their way toward a fundamental scientific understanding of photosynthesis processes. This will lead to improved biomass production, algal hydrogen production, and artificial photosynthetic processes.

During FY00-01 Bill Jacoby and Maria Ghirardi designed, fabricated, and operated an innovative photobioreactor to study the technical and economic feasibility of using a novel H_2-producing system as a commercial process for producing renewable energy.

Biological production of hydrogen by green algae is a potentially efficient source of clean, renewable energy. However, practical implementation of this system has been hampered in the past due to the extreme sensitivity of the hydrogenase enzyme to oxygen. Researchers completed an initial assessment of the potential of a novel algal H_2-production system to overcome these barriers to commercial production.

The experiments suggested that there is a process variable not being controlled which has a significant impact on the hydrogen yield, as well as strong interactions with other variables, giving the researchers insights to the next level of investigation that are being currently continued.

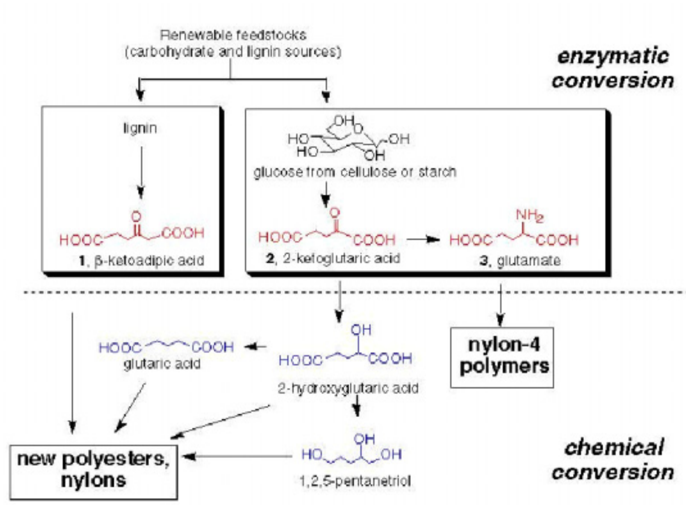


Figure 12. With their project, Joe Bozell and Steve Kelly showed that several important intermediate products could be derived from lignin and cellulose (two of the most abundant primary materials existing in biomass) and used to make poly-esters and nylons.

- Joe Bozell and Steve Kelley in FY00-02 demonstrated that the two most abundant raw materials in nature, carbohydrates and lignin, can serve as sources of important chemical building blocks, and demonstrated new conversion technologies. The research was specifically directed at addressing a technology gap in the efficient use of renewables as chemical feedstocks; i.e., addressing the lack of technological tools for the efficient conversion of renewables-based building blocks into products. The existing chemical industry is heavily based on "platforms" – key intermediates that can fan out into dozens of other products. The compounds investigated in this project are superb platform candidates in the context of a biobased products industry. Three starting materials (2-ketoglutaric acid, 2-methoxyglutaric acid, and 2-hydroxyglutaric acid), could be polymerized, and then the polymerization process was optimized and the materials were used to make polyesters and nylons. This research investigated the conversion of the building blocks into polymers and evaluated their commercial utility as platforms in a new biomass-to-chemicals industry. he researchers showed that NREL worked with researchers at the Pacific Northwest National Laboratory to combine PNNL's expertise in catalysis and biochemistry with NREL's expertise in polymers and chemistry. Together, the two laboratories established an overall core competency in polymer and chemical production from biomass, thereby positioning themselves to respond effectively to the national initiatives in biobased products and bioenergy.

2003 Developments:

- Research by Mark Davis aims to better understand the biological processes that determine the quantity and quality of energy and bio-based feedstocks. The team successfully analyzed hybrid Populus (poplar) and identified regions of the genome that contain genes that control carbon allocation (the distribution of carbon to stems, limbs, roots, etc.) and partitioning (cell wall chemistry), determining factors in feedstock quality and quantity. It appears that a small number of genes control carbon allocation, and they are independent of genes that control partitioning. The work also established proof-of-principle that cell wall chemistry impacts feedstock conversion efficiencies. The work resulted in the preparation of several papers and proposals, and additional funding was secured.

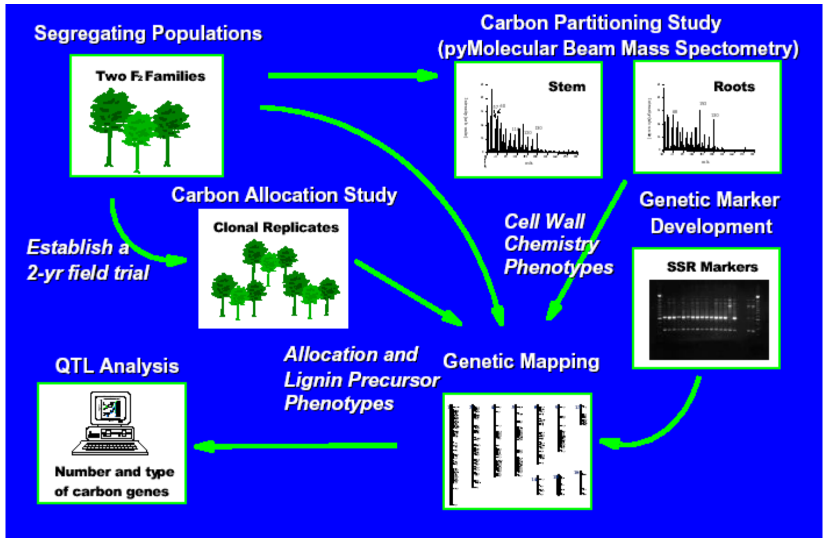


Figure 13. *Approach used by the Mark Davis team to map and analyze the genes that control the partitioning of carbon to stems, limbs, and roots of trees. Knowledge gained through this project may have significance for carbon management options – either the use of carbon to make products or the sequestration of carbon.*

- FY03 research led by Dan Dubois aims to develop stable catalysts for electrochemical reduction of CO_2 to CO, which will enable technologies for utilization of carbon dioxide and promote NREL's leadership role in the area of carbon dioxide utilization. The research aims to demonstrate increased catalyst stability by incorporation into thin films of ionic liquids. Work in FY03 included hiring a postdoc researcher, selecting ionic liquids, synthesizing the most stable catalyst studied previously, preparing a new ligand to promote catalyst stability, and beginning study of thin films with incorporated CO2 reduction catalysts. The team developed interactions with the University of Colorado, including writing a joint research proposal, that would be useful in the future for developing an NREL center for CO_2 utilization.

- Jim McMillan found that, despite the bioaugmentation appearing to offer a lower cost route to production of solutions with high target sugar(s) purity, chromatography remains a key separative unit operation. To date, there is still a tremendous amount of work that can be done to advance chromatographic separation of complex biomass hydrolyzates. While chromatographic approaches may not offer the lowest cost route for producing xylose- (or other biomass sugar(s)-)rich products, they nonetheless remain candidates for advanced hydrolyzate fractionation schemes. Chromatographic approaches such as SMBC have the distinct advantage of being able to produce high-purity biomass sugar(s) solutions without reacting away the other biomass sugars. Beyond this, with further work, it may be possible to optimize the operating parameters for SMBC to significantly reduce the estimated MXSP values for producing high purity xylose syrups using an SMBC-based process.

  Jim and his team also investigated the possibility of producing higher value products from xylose, i.e., those that could justify a higher purchasing price for xylose syrup substrate(s). Unfortunately, identification of higher-value products other than xylitol (which has an existing but relatively small market) for which the value proposition makes sense remains challenging. While many products can be made from xylose, production attributes using xylose are generally inferior to those using glucose. Thus, xylitol remains the only known product for which a relatively high product value makes it economically feasible to purchase xylose at relatively high prices (>> 10¢/lb). For all other products examined to date, inexpensive glucose is the traditional carbon source, and there are insufficient production process or product performance quality improvements using xylose to justify switching the sugar substrate. Using xylose rather than glucose in such types of cases only makes the value-added production processes less economical.

Jim's group also exploited Biological Specificity to Improve Purification Economics. The researchers attempted to develop and partially reduce to practice the concept of bioaugmented separations. While absolute performance results require an appropriately selective microbial strain to be identified or developed, the proof of concept experiments showed very effective purification of several biomass sugars in selected binary, ternary, and more complex sugar mixtures, i.e., biomass sugar mixtures representative of the types that could be available as slipstreams from integrated lignocellulose biorefining facilities employing enzymatic cellulose hydrolysis "sugar platform" technologies. Using existing strains is sufficient to enable the sugar purity of a target sugar or group of sugars (e.g., pentoses) to be increased from 35-50% to 75-95% and even 100% in some situations. Despite these confirmatory and encouraging experimental results, it remains to be determined whether or not the limited results produced will be sufficient to develop a strong patent application. Review by NREL's Patent Management Committee in early FY04 is expected to resolve this issue.

This project provided a good foundation for initiating biorefinery R&D, and helped NREL to begin several useful collaborations related to increasing NREL's biomass process stream-related separations capabilities. For example, this project facilitated contacting and starting collaborations with Amalgamated Research, Inc. This collaboration has already led to information sharing as well as two joint proposals being authored and submitted. By anticipating the sugar platform multiproduct biorefinery concept, this project also helped advance the Biomass Program's thinking about and analysis of lignocellulose- and sugar platform-based biorefineries. For example, it helped position NREL to put together RFPs related to developing biorefinery analysis tools. It is critical to continue to fund projects of this type to foster multiproduct biorefinery development.

- David Dayton worked on identification of the forms of nitrogen in biomass, and the kinetics of the transformation of fuel-bound nitrogen to NOx, which would allow these chemical details to be input to DFD models to aid in developing new methods for NOx control and modifying biomass thermochemical conversion processes to optimize NOx reduction. A basic understanding of NOx formation during thermochemical processes can justify increasing the use of biomass for electricity production while meeting or exceeding present and future federal NOx emission standards. In FY03, preparations were made for biomass combustion experiments. Labeled alfalfa has been received and is being prepared for experimental use.

- The composition of feedstock material is a primary determinant of process yield in biomass conversion and combustion/pyrolysis technologies, and yield is a major driver in process economics, the ability to control or manage biomass composition is important to commercialization of this technology. Obtaining a detailed knowledge about the set of genes in plants that impact cell wall composition and architecture could be useful tools to breed or genetically engineer crops for improvement of biomass-based process economics. Identification of this set of genes in plants provides a means for determining the functional role of those

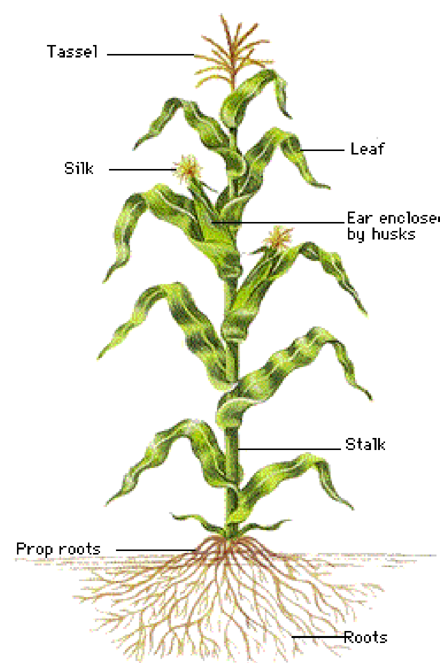


Figure 14. *In this project a team led by Steve Thomas used near-infrared (NIR) spectroscopy and multivariate analysis to develop a method for screening corn plants for differences in cell-wall composition, and to explore the possibility of using NIR spectra of corn leaves to predict the chemistry of corn stover and leaf tissue.*

genes in plants (i.e., functional genomics) and contributes to the development of a plant biotechnology capability at NREL. In FY02-03 work led by Steve Thomas showed that near infrared spectroscopy can be used effectively as a high throughput primary screening tool in plant genetics. NIR spectroscopy can be used to identify individual plants with unusual cell wall compositions, significantly reducing the number of candidate lines under consideration. The techniques developed in this project can be used to identify lines that carry mutations in genes that are involved in cell wall metabolism, a first step towards cloning and characterization of such genes.

- Min Zhang strived to identify or create better transporters that are highly efficient at transporting sugars and expressing them in ethanol producing microbes. As very little is known about the structure-function relationships of pentose transport proteins, it is difficult to predict if transport activity can be improved by expression of modified transporters in microorganisms. In FY03, relevant literature was reviewed and steps were taken to identify a postdoctoral candidate to conduct the project.

- Mark Nimlos explored and developed biomass thermochemical conversion technologies to convert biomass to electricity, fuels, and chemicals via three main pathways: pyrolysis, gasification, and combustion. Collecting detailed quantitative information is a crucial step toward the commercialization of biomass thermochemical conversion technologies. This information can be used to help identify promising pathways and assist in reactor design and scale up. This research project is developing a new experimental technique capable of collecting quantitative kinetic information on thermochemical conversion processes far more rapidly than is currently possible.

  In FY03, the team conducted experiments in thermal degradation of allyl ether to acetaldehyde and propene to help determine the experimental uncertainty of residence times and temperatures. The team conducted additional experiments of thermal decomposition of diethoxy methane (a model compound containing an acetyl group), laevoglucosan (an important intermediate in the pyrolysis of cellulose.) Experiments in the thermal decomposition of gallium compounds may help understand important reactions in the formation of thin film photovoltaic devices using organic chemical vapor deposition.

  Expanding NREL's capabilities in Computational Fluid Dynamic modeling, researchers will apply these computational methods to measure reaction kinetics in a pulsed micro-reactor at time scales much shorter than achievable in other continuous flow reactors. This project will begin the process of establishing NREL as a world leader in computational methods and experimental techniques for determining accurate, quantitative kinetics for biomass thermal conversion processes. The results will aid in optimizing existing processes and help facilitate the successful scale up and commercialization of developing processes.

- Mark Davis conducted the proof-of-principle hydrolysis experiment that demonstrated that changes in cell wall chemistry can significantly enhance the conversion efficiency of the derived biomass feedstocks. These results substantiate the concept that fast growing hybrid poplar are suitable to manipulation through traditional breeding and/or genetic engineering to enhance their value as a source for renewable feedstocks while at the same time providing a resource that could be used to improve the soil sequestration potential through the non-harvested portion of the plant. In FY03, the team established inter-laboratory expertise in poplar genetic mapping as it relates to energy and bio-based feedstock quantity and quality by analyzing hybrid poplar families and identifying genetic markers linked to these processes.

- The work of Arjun Singh and Mark Davis addresses several key questions in identification of microorganisms that can efficiently produce ethanol and other products from biomass. First, can metabolic pathways be identified which are bottlenecks in the production of ethanol or other bioproducts? Secondly, what improvements can be made in the metabolic flux through these identified bottlenecks? Finally, since microorganisms are exposed to harsh environments during biomass utilization, what effect does exposure to a wide variety of compounds and growth conditions have on the cell's metabolism and how are these effects reflected in production yields?

Genome sequencing and the production of gene maps have far out-stripped the ability to rapidly discover and annotate the function of unknown genes. After a genome is completed, roughly one-third of the genes are identified as similar (by protein sequence only) to known genes in other organisms while an additional third is completely novel. The methods developed with this project will create a new tool for assigning gene function within the metabolic pathways.

The project employs recent advances in metabolomics, a new field that examines the metabolic state of a cell *in toto* and can be used to determine kinetic flux through pathways as well as the pool size of the metabolites themselves. From this information, a model of the cell's metabolism can be established. The methods developed will be instrumental in quickly determining the metabolic state of a fermentation culture during biomass utilization as well as in the selection of higher production microorganisms. In FY03, a library of yeast gene deletion strains was identified and is in the process of being purchased. Follow-on project funding was obtained, a proposal was submitted to an Interagency call on metabolic engineering, and offers were expended for postdoctoral positions in this project.

- Many industrial processes based on biomass feedstocks would benefit from low cost and environmentally friendly methods of lignin removal. The goal of Mike Himmel's project was to validate a lignin-depolymerizing enzyme that had the potential to redefine many biomass-based technologies. Unfortunately, the group and collaborators were unable to confirm the existence of the enzyme or gene. However, the work developed considerable capability in growing and inducing white rot fungi, which is effective at degrading lignin. The work also developed a new capability for NREL in characterization of lignin by light scattering methods (HPSEC-MALLS), which will be used to continuen the search for a lignin-depolymerizing enzyme.

  The baseline understanding and tools developed at NREL during the course of this project have resulted in the submission of two grant proposals in collaboration with industry in response to the recent USDA-DOE Biomass R&D Solicitation. Researchers have also made numerous presentations at international scientific meetings reporting the HPSEC-MALLS approach to determining lignin depolymerizing activity and are currently preparing several manuscripts based on this work.

- Kim Magrini and Robert Evans explored carbon sequestration in the terrestrial biosphere, more specifically the storage of carbon in plant biomass and soils. Soil organic matter (SOM) comprises an especially large pool of carbon in many ecosystems and there has been increasing emphasis placed on enhancing carbon sequestration in this pool through timely manipulation of agricultural and forest lands. Existing methodologies for measuring the carbon in SOM are time-consuming and expensive which are serious limitations, as they often require extensive replication or order to identify statistically significant differences between or among treatments. In addition, efforts to characterize SOM have also been limited, are time consuming, require destructive sampling, and thus often preclude broad-scale application across a range of sites.

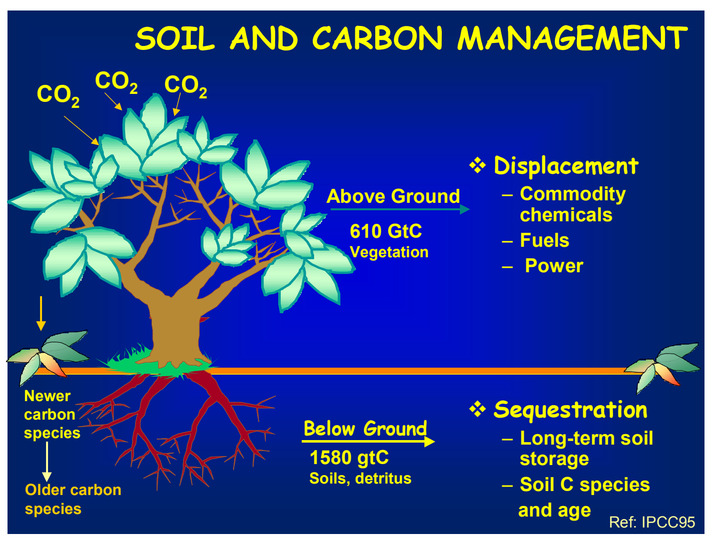


Figure 15. *Through their DDRD project, Kim Magrini and Robert Evans, developed a method to rapidly analyze the carbon in soil through the use of molecular beam mass spectrometry and multivariate analysis. This has strengthened NREL's capabilities in carbon management and soil carbon sequestration.*

The researchers are using NREL's expertise in molecular beam mass spectrometry (MBMS) and multivariate statistical analysis to characterize soil organic matter, as well as correlate and complement the results with NREL solid-state NMR and ORNL Raman soil analysis. The aim of the research is to develop rapid and comprehensive analyses of soils that will allow a better understanding of specific scientific issues, and use this technology for measurement and monitoring.

The fundamental research and development of this analytical capability will centrally position NREL as the lead lab in rapid soil analysis within the National Bioenergy Center and the Forest Service Northern Global Change Program.

Work in FY03 analyzed degraded loblolly pine roots and nearby soils, their componenets, age and root inputs to the soil over time. Analysis of Tionesta forest soils demonstrated the capability to distinguish hardwood from softwood soil carbon inputs at a distance from the tree. Work continues on modeling of SOM content and other soil characteristics. The team achieved considerable visibility for this work through published papers and presentation, and collaborations were initiated with the US Forest Service, Boise Cascade, and the University of Tennessee.

- Pin-Ching Maness has investigated how carbon monoxide (CO) is oxidized to CO_2 in the water-gas shift reaction performed by several photosynthetic bacteria. Understanding this process could lead to the ability to manipulate CO to maintain high rates and duration of the shift reaction, which could lead to the development of a bioreactor for the long-term processing and mitigation of CO gas. A goal is to develop a protocol for purifying CO hydrogenase (CODH), an important protein regulating the oxidation of CO. Technical accomplishments include developing the protocol for purification of CODH and improved understanding of the role of CO as an inducer, initiating the synthesis of new proteins required in the CO oxidation reaction. The results support the conclusion that with CO serving as the inducer, its constant presence is necessary to maintain oxidation activity at high rate and long duration.

Advanced System Design and Analysis

Successes in the past five years:

- In FY99 Mark Mehos successfully designed, installed, and tested a small-scale concentrating parabolic dish, the first prototype of a design that could ultimately (at moderate production levels) meet cost, performance, and reliability goals necessary for successful commercialization of concentrating solar power (CSP)-related technologies in remote markets.

  An analysis performed in 1999 by staff within NREL's Center for Buildings and Thermal Systems indicated that remote markets for CSP technologies were worth pursuing due to the large size of the markets and potentially favorable economics. NREL has a recognized expertise in designing large parabolic dish concentrators that are used in conjunction with Stirling engines to convert the heat of concentrated sunlight into 25 kW of electric power or more.

  This project addressed the technical feasibility of designing and fabricating small-scale (5-10m^2) concentrating systems for application to remote markets; i.e., small dish concentrators that can be used with a variety of converters—such as high-efficiency PV cells—to generate from 1kW to 3 kW of power

  The researchers demonstrated a proof-of-concept for the technical feasibility of designing small dish concentrators that can be used with a variety of converters – such as high-efficiency PV – to generate power.

- In FY99-00 James Tangler verified the predicted performance of advanced airfoils for high-efficiency cooling fan blades. The research hypothesized that improved NREL-designed airfoils would reduce the power requirement for cooling tower fans by 2%-5% relative to current technology, thereby improving energy efficiency. In the previous projects researchers used their expertise in wind turbine technology to design airfoils for cooling tower blades, with the expectation that the design would significantly reduce the power requirements for cooling tower fans. In this project they verified significant energy savings provided by NREL's advanced airfoils for medium sized cooling tower fans. The research strengthened NREL's existing advanced airfoil design core competency and provided the cooling tower fan industry with airfoils for more efficient sized blades.

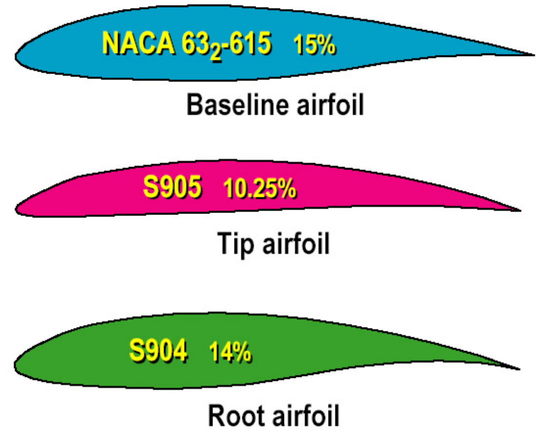


Figure 16. *Jim Tangler's specially designed airfoils significantly increased the efficiency of cooling-tower fan blades by increasing the thrust of the blades (relative to baseline) and reducing drag.*

- In FY99-01 Scott Ward used recently developed processing techniques to design and fabricate mini-modules from the GaInP/GaAs tandem device structure developed by NREL's high-efficiency PV team for use under high flux provided by dish concentrator systems. The scope was expanded to include investigation of the feasibility of employing the record-breaking GaInP/GaAs/Ge triple-junction solar cells for this application.

  Researchers explored the concept of connecting III-V multi-junction solar cells monolithically, in series on a non-conductive substrate to make mini-modules that can be used under high solar concentration. This could lead to a next-generation technology that combines solar thermal concentrator technology with high-efficiency PV technology to produce inexpensive electric power systems.

  Researchers designed a small, high-efficiency PV cell with the structure and material properties that will enable it to operate appropriately under the spectrum and high flux levels of dish solar concentration. They also worked out the processing complications associated with applying these ideas to multi-junction PV systems, and they demonstrated high-performance discrete converters.

- In FY99-01 Jim Ohi defined and established a leading role for NREL in the basic science, design, development, and validation of the next generation of fuel cell systems.

  This project created a unique capability at NREL in fuel cell science and technology, from fundamental theory to materials science that provides a foundation for a fuel cell RD&D program at NREL. The project linked existing areas of technological excellence at NREL, including high-level quantum mechanical theory and modeling, electrocatalysis, and materials research and characterization.

  By studying oxidation pathways in detail with fundamental theory, NREL now has a data bank of information that can guide catalyst and other material development. A rapid throughput screening process based on combinatorial synthesis for new electrocatalysts was successfully adapted for the research project, and more than 20 metal oxide nanoparticles as well as Schiff base complexes were screened. Although no new candidates were immediately revealed through this process, some promising possibilities for further research were identified.

  Research determined that a direct ethanol proton exchange membrane (PEM) fuel cell is technically feasible but will require additional work to develop the necessary non-precious metal catalysts and higher temperature membranes; and significant progress was made in identifying and isolating the key R&D that needs to be done to achieve direct oxidation of ethanol in a PEM fuel cell. In addition, the researchers were able to demonstrate the feasibility of applying high-purity single-wall carbon nanotubes in key PEM fuel cell components.

Researchers also assembled a fuel cell test station that will allow NREL to test new catalysts, new membranes, and new membrane-electrode assemblies. The research team also recommended an NREL fuel cell R&D strategy for consideration by NREL management.

- In FY00-01 Chris Gaul demonstrated the feasibility of producing a combined refrigeration compressor and liquid refrigerant pump inexpensively enough to be practical wherever it is technically desirable. Refrigeration and air conditioning consume 15% of U.S. electric power. This project will develop an advanced prototype of a combined refrigeration compressor and liquid refrigerant pump to lower the cost of energy-saving cooling designs. Lower cost leads to expanded use and lower national energy consumption. While the product is aimed at a niche market, even a small piece of a $40 billion worldwide refrigeration and air conditioning market will have a substantial impact.

- In FY01-02 John Pern developed new kinds of encapsulant materials or formulations that can be extruded into films or sheets, that are convenient to handle, and that are suitable for ambient (non vacuum) lamination and encapsulation of crystalline silicon and thin-film PV modules.

This research was designed to address head-on a critical bottleneck in a photovoltaic manufacturing process that is manifested by a labor-intensive vacuum-lamination encapsulation method using ethylene vinyl acetate. The researchers were developing new kinds of encapsulant materials or formulations that can be extruded into films or sheets that are convenient to handle and suitable for ambient (non-vacuum) lamination and encapsulation of crystalline silicon and thin-film PV modules. The combination of a non-vacuum ambient encapsulant with a heated-press lamination/encapsulation process would enable a substantial reduction in labor requirements, energy consumption, and cost of encapsulation equipment. It could also lead to process automation, resulting in a large increase in production speed and yield. With higher performance, more durable encapsulants, and a lower cost encapsulation process, the U.S. PV industry will be in an advantageous position in global competition.

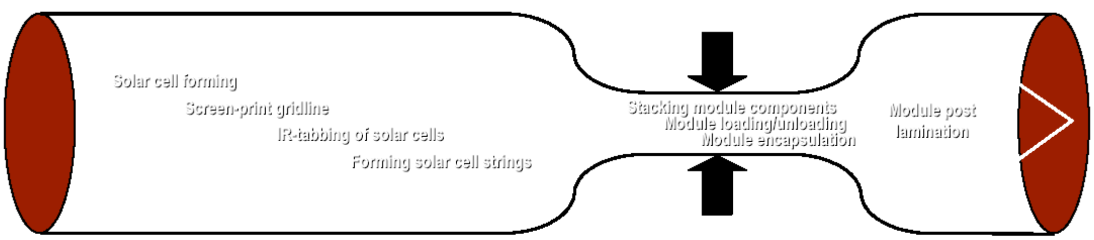


Figure 17. *John Pern's research sought to eliminate a bottleneck for PV manufacturing by developing a new kind of encapsulant that can be extruded into films that is suitable for ambient (non-vacuum) lamination and encapsulation.*

The researchers successfully developed new kinds of encapsulant materials and extruded those materials into films that were used for ambient lamination of silicon solar cells. The lamination was bubble free and had good optical and adhesion characteristics. Accordingly, the researchers successfully met the key objectives of the project. However, the new ambient-processible formulations and processing procedure and conditions remain to be optimized. In addition, equipment and tools specifically for PV module encapsulation in the ambient have to be designed and developed.

- During FY02 NREL's scientist Desikan Bharathan worked on reducing the parasitic power consumed by forced air fans for air-cooled heat rejection systems to the ambient air. Researchers examined methods to use the energy contained in the hot exhaust stream and thus reduce the required fan power to induce airflow in heat exchangers. Using limited height towers and utilizing the energy of rising hot air can reduce the required fan power. This concept can lower the cost of power generation by lower temperature power systems such as geothermal and solar thermal power. The technology also has the potential to reduce energy consumption of tall buildings.

Energy Analysis

Successes in the past five years:

- In FY98-01 Brandon Owens and Sam Baldwin tested the hypothesis that providing real-time, on-line mechanisms to test model assumptions will fundamentally advance the way policy analysis is performed by enabling policy analysts to interact with stakeholders in developing consensus on model assumptions, and ultimately on preferred policy options.

  In the 1990s, the emergence of the Internet initiated a fundamental transformation in the way that energy analysis is conducted and communicated. Institutionally dispersed analysts are beginning to achieve unparalleled results through on-line collaborations with remote colleagues. Formerly unaided decision-makers are now becoming equipped with specialized knowledge and capability through the proliferation Internet-based analysis applications. And previously uninformed stakeholders are opening themselves to the wealth of possibilities offered by Internet-based information dissemination.

  NREL made a strong commitment to becoming a leader in the emerging field of Internet-based energy analysis, or e-Analysis, by funding the Technology-Policy Expert System.

  NREL’s internet-based capability allows analysts to collaborate on-line with remote colleagues and to evaluate the effectiveness of renewable energy policy. NREL’s Renewable Energy Analytic Studies Network provides the basis for establishing a standard of practice in energy analysis. REASN is becoming the gateway to the analysis applications developed within this effort.

  As of September 2001, preliminary evidence from application logs and user surveys indicated that the applications developed as part of this effort have indeed begun to fundamentally transform energy analysis. Additional information will be collected over the next several years to make a final determination on the long-term impact of this new analytical approach.

- Research conducted by Bill Marion during FY00 assisted NREL with development of a new capability for creating multi-year data sets of hourly solar radiation and meteorological data for locations throughout the world. Users can now size and evaluate the performance and economics of renewable energy systems thereby reducing the risk in the deployment of renewables and aiding in the selection of the best renewable technology for a specific location.

  This research provided NREL with a new capability, unmatched by any other organization, for developing worldwide weather data sets. The capability to develop hourly data sets and their associated products enhanced the Laboratory’s ability to address the potential for technology deployment by providing the necessary weather data for performance and economic analyses of renewable energy systems for virtually anywhere in the world.

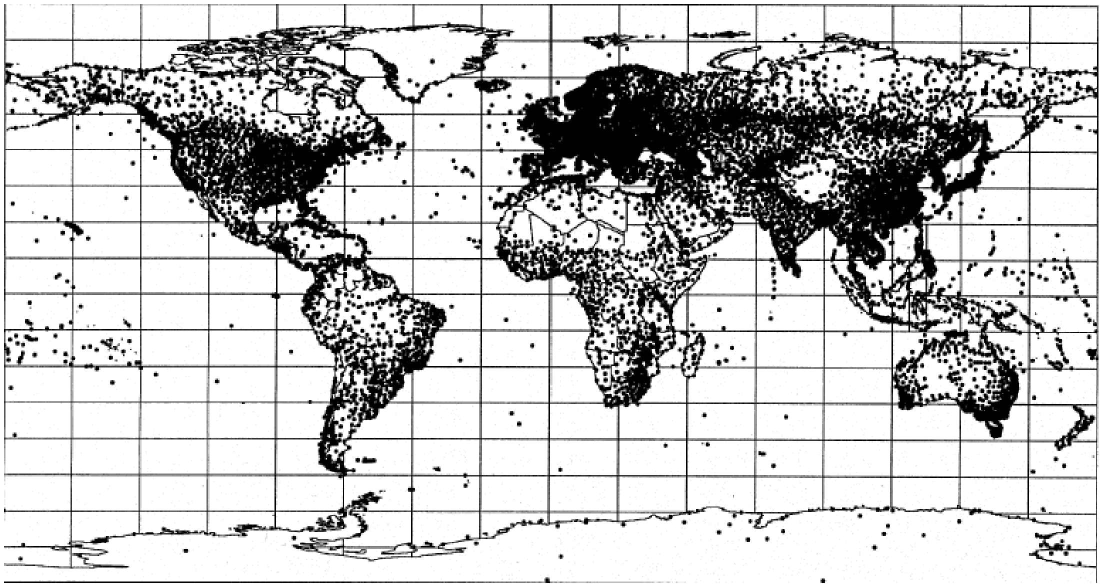


Figure 18. *Bill Marion's project compressed weather data from 20,000 DATSAV2 stations from around the world and saved it on DVD. This allows rapid access to the data (cutting access time from days to seconds) and enhances the ability of researchers to model solar radiation from these weather records.*

NREL researchers merged rapid-data-access technology with their abilities to model solar radiation from weather records and to fill-in missing data. This enabled them to produce worldwide hourly input to computer programs that simulate the performance of a wide variety of renewable energy systems.

- In FY01-02 Peter Lilienthal enhanced Hybrid Optimization Model for Electric Renewables (HOMER™) software for grid-connected applications.

The rapidly increasing interest in small, modular generation that can be connected to the grid at distribution voltages creates a significant window of opportunity for many renewable energy technologies (RETs). Unfortunately, RETs will be disadvantaged in this market by the additional analytical complexity that is required to understand the role that they can play.

In particular, two of the most important RETs, photovoltaics and wind, are non-dispatchable and have resource availabilities that vary substantially over time and location. Much of the distributed generation market is concerned with reliability, such that it is necessary to analyze RETs that are integrated with dispatchable fuel-fired technologies in a hybrid configuration.

The HOMER software has unique capabilities to optimize among very large numbers of permutations of hybrid designs, perform sensitivity analyses across wide ranges of market conditions, and perform hourly simulations of time-varying resources. Without an analytical tool that makes these capabilities easily accessible to distributed-generation decision-makers, the market will favor the more easily understood fuel-fired technologies.

NREL now has a model for comparing distributed generation technologies that is unparalleled in capability, particularly with regard to the modeling of renewable technologies. The HOMER software will help renewable energy technologies compete in the marketplace by removing the analytical barrier that had existed by virtue of increased difficulty of analyzing renewable technologies.

2003 Developments:

- In 2003 Walter Short at NREL has been developing renewable-energy-specific models for wind and PV. While these will be useful for DOE analysis, there is a strong need to adapt what is learned from these NREL modeling efforts to other existing energy market models. NREL will need to develop tools for the web to do this. This project will develop such tools and ensure their use within the energy modeling community. Progress in FY03 included developing a web page prototype and initial wind supply curves including transmission costs based on GIS analysis. Funding is expected in FY04 for completion of the photovoltaic model, using NREL's WinDS model, and the expansion of the WinDS model to include hydrogen. Three modeling groups contacted NREL desiring collaboration on the subject work.

Hydrogen Production, Delivery, Storage, Use and Infrastructure

2003 Developments:

- FY03 work by Tony Markel sought to quantify the benefits and opportunities for controlling the composition of inlet gases to fuel cell system within an automotive application, to quantify the potential for system cost, mass and volume reductions. The work will help define the general operating characteristics required of an oxygen supercharging device to improve fuel cell performance on an "as needed" basis over typical driving profiles. Accomplishments included a literature review, revisions to the fuel cell system model to respond appropriately to changes in oxygen partial pressure, and preliminary vehicle simulations that support expectations that an oxygen supercharged system can improve fuel economy on aggressive driving profiles.

- Water-splitting, a key part of the photosynthesis process that provides the earth's atmospheric oxygen, is not nearly as well understood as other aspects of photosynthesis. Better understanding of this process will support all bioenergy approaches to producing renewable fuels including NRELS's algal H_2-production approach. Mark Siebert's work in FY03 yielded exciting information about the donor side of Photosytem II and will provide tools for increased understanding of the water-splitting apparatus and the processes it catalyzes. The work resulted in publishing and preparing several papers and a funding proposal, as well as collaborations with Moscow State University.

- Stefan Czernik and Pin-Ching Maness studied pretreatment technologies, which may speed up the direct utilization of biomass by microbes. All currently available pretreatment technologies often release lignin degradation byproducts that are biocidal to the microbes. NREL applies a thermo-mechanical steam pretreatment of biomass that solubilizes hemicellulose and makes the cellulose microstructure more accessible to anaerobic microorganisms. Both solid and liquid fractions from the pretreatment are then exposed to microbial consortia under anaerobic, thermophilic condition to produce H_2 and CH_4 from carbohydrates while also generating a lignin-derived end product suitable for use as compost or fertilizer. In FY03, sewage sludge from the Denver waste Water Treatment Plant was proved to contain a rich mixture of microbes capable of producing hydrogen from glucose fermentation. Thermophilic microbes are present in sewage sludge which produce hydrogen from glucose at 55C. It was determined that repeated glucose feeding is necessary to sustain hydrogen production. Optimal amounts and frequency of glucose feedings for maximal hydrogen production were determined. The team achieved hydrogen yield from glucose at 50% of the theoretical maximum. Preliminary studies indicated that microbes in sewage sludge are capable of using cellulose directly to support hydrogen production, although for shorter duration. Heat shock treatment was proved to be effective at inactivating methanogen from converting hydrogen into methane. A proposal for further research in the area was submitted to the DOE hydrogen, Fuel Cells and Infrastructure Technologies Program.

NREL's DDRD Program plays the important role by enabling the movement of science and engineering ideas from knowledge creation to knowledge adoption. The examples highlighted above demonstrate the evolutionary nature of this process, and the role of the DDRD Program within it. DDRD projects significantly advance research and development directed toward solving nation's present scientific and technical priorities, and also serve the purpose of determining the merit and utility of new, innovative concepts and ideas.

Appendices

Appendix A. Program Projects

Advanced Materials for Energy Efficiency and Renewable Energy Technologies

Project Title: **Electronic Communication in Assemblies of Semiconductor Nanoparticles**

Principal Investigators: **Jao van de Lagemaat & Helio Moutinho**
Performance period: 05/03 – 04/05
Award: $300,000
Status: In progress

Goals:

- Establish NREL capability to investigate current transport in arrays of semiconductor quantum dots and to link these properties to the energetic properties of single particles.
- Provide a framework for connecting electronic communication in a macroscopic film of interconnected nanoparticles with the energetic structure of isolated quantized nanoparticles. Extend the diagnostic capability at NREL to characterize the energy levels of nanostructure matter and to study interparticle charge transport dynamics in nanoparticle arrays. A significantly expanded insight into the interplay between the energy structure of a single particle and inter-particle transport is anticipated. It is also expected to lead to peer-review publications and proposals for outside funding.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - The project was re-scoped to pertain to quantized semiconductor nanoparticles.

   - Dr. Olga Miçic (NREL) has agreed to provide samples of quantized III-V and II-VI semiconductor nanoparticles.

   - A supplier was found for interdigitated electrodes that can be used for the electrochemical transistor measurements. A possibility of making these interdigitated electrodes internally, using photolithographic techniques available at NREL, is under investigation.

   - A new AFM/STM machine was installed in the FTLB that will be used for the room-temperature tunneling spectroscopy measurements and for the characterization of the nanoparticle monolayers.

   - A new low-temperature AFM/STM machine has been ordered and will arrive at NREL at the end of 2003. This machine will be used for the cryogenic measurements under UHV conditions that were proposed.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

    - Jao van de Lagemaat (coauthors Helio Moutinho and Arthur Frank) presented a talk on "AFM and STM Studies of Monolayers of Ultrasmall Anatase TiO_2 Nanoparticles" at the Gerischer symposium of the 203rd meeting of the electrochemical Society in Paris, France April 27-May 02, 2003.

3. **Resources:** (facilities, staff, equipment, etc.)

4. **Collaborations:** (partnerships, sub-contracts, etc.)

    - A new collaboration was started with Prof. D. Vanmaekelbergh at Utrecht University, the Netherlands to simulate charge transport in disordered arrays of quantum dots.

Impact/Significance:

This project introduces a unique approach that combines three interrelated diagnostic techniques (low-temperature and ambient tunneling spectroscopy, photocurrent transient spectroscopy, and electrochemical transistor setup) for characterizing the energy levels of individual quantized semiconductor nanoparticles and the dynamics of interparticle charge transport in assemblies of these nanoparticles. The combination of these techniques is expected to yield insight into the interplay between the energy structure of a single particle and interparticle transport. The research also involves the synthesis and characterization of dispersed nanoparticles and their assemblage as monolayers and multilayers.

Proposed Next Steps:

- Generate monolayers and multilayer assemblies of the colloidal quantum dots and study these using AFM and STM.
- Use time-resolved photocurrent spectroscopy to characterize the rate of charge transport between substrate and adsorbed particles and between adsorbed particles.
- Use the electrochemical transistor to characterize charge transport in the assemblies.
- Use tunneling spectroscopy to resolve the energy levels of single particles.

Project Title: **OWLEDs: Next Generation Indoor Lighting Using Organic White Light Emitting Diodes**

Principal Investigator: **Sean Shaheen**
Performance period: 04/03 – 03/05
Award: $500,000
Status: In progress

Goals:

- Establish NREL capability in developing organic and nanostructured materials for use in high efficiency organic solid state lighting.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

- Polymer morphology: We have been investigating the dependence of the charge transport in conjugated (electronically active) polymer films to the morphology (nanoscale structure). Specifically, we have studied the effect of thermal annealing of the films on the charge carrier mobilities of the holes (positive charges). We have found that the hole mobility increases upon annealing for short times (~ 2 minutes) but then decreases for longer anneal times. This was found to be true for two important polymers studied, OC1C10-PPV and P3HT. These polymers have drastically different glass transition temperatures (200 ºC and 25 ºC respectively), however they both show enhanced mobilities upon annealing. This suggests that the phenomena may be a general one for many types of conjugated polymers. Preliminary FTIR spectroscopy of the film pre- and post-anneal reveal small changes in the morphology upon annealing.

- Nanostructured composites: Recent advances, both at NREL and in the field in general, have brought nanostructured semiconductor oxides to a prominent position in materials research. Novel nanostructures have been demonstrated from semiconductors such as TiO_2 and ZnO using very low-cost, solution-based synthesis. The ease with which these nanostructures can be made makes them attractive as materials for organic – inorganic composite materials for semiconductor device applications. We have succeeded in making composite materials consisting of mesoporous nanostructures of TiO_2 intercalated with conjugated polymer. These composites show good filling of the porous TiO_2 structure with the polymer, which is a promising first step toward making devices from these materials. We have also been working with nanostructured ZnO nanofibers. These nanofibers are grown as a 'nanocarpet' with a common fiber orientation that is perpendicular to the conducting oxide substrate substrate. This is a very promising structure for device applications, as the ZnO nanofibers have a very high electron mobility. Also, such structures can act as optical scattering media. This is important because a major loss mechanism in OLEDs. Approximately 80% of the light generated in the active layer of and OLED is typically lost to waveguiding out the sides of the device. A scattering medium, such as the ZnO nanofiber array, can counteract this problem. We have begun making polymer / ZnO nanofiber composites with promising initial results.

- Interfaces: An important aspect of nanostructured composite materials is the interface between the oxide and the polymers. The character of this interface determines the wetting (degree of contact) between the polymer and the oxide, as well as the electron transfer rate between the two materials. We have been investigating the effects of attaching molecular binding groups (surface adsorbates) to the oxide prior to introducing the polymer into the structure. Kelvin probe surface photovoltage measurements show that binding groups attached to TiO_2 are effective at quenching trap states that are known to be present on the surface. The net result of the binding groups is to enhance the charge transfer characteristics of the interface.

- Optical modeling*:* In order to optimize polymer device development, we have worked on measuring the dielectric constant of the relevant optical layers for these devices, and on modeling the optical processes that occur during light generation.

  In addition to the measurements of polymer films, we have begun preliminary investigations into the optical properties of the nanostructured oxide / polymer composite materials discussed above, with the aim of designing structures that yield enhanced forward light output of the devices.

- Molecular modeling***:*** A crucial aspect of the development of a real organic semiconductor effort at NREL is the capability to design and synthesize new organic molecules and polymers. The field of organic semiconductors is very different from conventional semiconductors in the sense that there are virtually an infinite number of organic molecules that one can consider synthesizing and using in a device. In conventional semiconductors, the palette of atomic species that one can choose from is quite small, and most of the science and engineering is in depositing those atomic species in an optimal way.

  We have begun preliminary computational studies of the relationship between the structure of an organic molecule / polymer and its electronic /optical properties.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

- Brabec, C.J.; Nann, T.; Shaheen, S.E. "Nanostructured p-n junction for printable photovoltaics", to appear in the *Materials Research Society Bulletin*, Jan. 2004.

- Breeze, A.J.; Rumbles, G.; Gregg, B.A.; Ginley, D.S. "The effects of processing conditions on polymer photovoltaic device performance", *Proceedings of the SPIE,* National Meeting, San Diego, Aug. 2003.

- Shaheen, S.E. "Nanostructured oxide / conjugated polymer photovoltaic devices", SPIE National Meeting, San Diego, Aug. 2003.

- Shaheen, S.E.; Ginley, D.S. "Photovoltaics for the Next Generation: Organic Based Solar Cells", to appear in the *Dekker Encyclopedia of Nanoscience and Nanotechnology*, Marcel Dekker, New York.

- Shaheen, S.E.; Gregg, B.A.; Ginley, D.S.; Rispens, M.T.; Hummelen, J.C. "Surface state quenching and charge transfer enhancement at the Ti02 / conjugated polymer interface using surface adsorbates", in preparation for the *Journal of Physical Chemistry B.*

- Wang, Q.; Shaheen, S.E.; Williams, E.L.; Jabbour, G.E. "Hybrid organic-inorganic photoconductive diode", *Appl. Phys. Lett.* 83, (2003).

- We are currently pursuing a large funding opportunity through the Department of Defense's DARPA program. They have announced a program on "Organic, Nano-structured, Flexible Photovoltaics." We have submitted proposals to this call through a number of industrial lead teams. These industrial leads are Konarka Technologies, General Atomics, and Spectrolab. The proposals have NREL budgeted at between \$100K–-\$300K per year for 5 years. This is a major opportunity to enhance the organic semiconductor program at NREL, and to provide funding for new equipment purchases and potential new hires to promote organic semiconductor device development of all types, including OWLEDs for solid state lighting.

- Also, we are awaiting information on a major initiative through the DOE to fund solid state lighting. This initiative is awaiting congressional approval.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

- William Mitchell has been hired as the postdoc to perform synthetic chemistry. He is graduating from Oxford University in the UK, and will begin ~ November 1.

- Ordered a dry box for fabrication of the devices in an inert atmosphere, which should arrive shortly. This will allow us to work with low work-function metals and air sensitive interfacial dopants that provide efficient electron injection.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

   - Prof. R. T. Collins, Dept. of Physics, Colorado School of Mines

   - Prof. M. McGehee, Dept. of Materials Science, Stanford.

   - Prof. J. C. Hummelen, Dept. of Chemistry, University of Groningen, the Netherlands.

   - Prof. G. E. Jabbour, Optical Sciences Center, University of Arizona

   - Prof. N. S. Sariciftci, Physical Chemistry Dept., University of Linz, Austria.

   - We have CRADAs in place, or nearly so, with Microfab Technologies, Inc. (Plano, TX) and Konarka Technologies, Inc. (Lowell, MA). Microfab is a leading inkjet company that recently obtained SBIR funding to print polymer based semiconductor devices via their technology. We have begun collaborating with their team in fabricating polymer films and devices. Konarka is a leading organic semiconductor device start-up company specializing in photovoltaics. They have developed a number of technological innovations that can be directly applied to large area light applications. We are working with them on producing optical device structures using a variety of novel material sets.

Impact/Significance:

Proposed Next Steps:

- With the polymer annealing project, develop a better understanding of the morphological changes that are taking place in the polymer films upon annealing.
- In the area of nanostructured composite devices, optimize the overall morphology and beginning to make functional devices using the composite materials. Incorporate the surface binding groups onto the oxide interface to improve charge transfer between the inorganic and organic components, with the aim of increasing device efficiency.

- Make nanostructure composites that reduce wave guiding and are effective at scattering light out the front of the device.

- In the area of molecular modeling, begin investigating more novel molecular structures, and to narrow our search to some specific families of molecules.

- Begin synthesizing these compounds.

- Look at the mechanism of triplet harvesting in OLEDs using quantum dots.

- We will then be able to fabricate highly efficient devices that are on par with the rest of the research community.

Project Title: **Improved Thermoelectric Materials Based on Quantum Dot Superlattices**

Principal Investigator: **Mark Hanna**
Performance period: 05/03 – 04/05
Award: $200,000
Status: In Progress

Goals:

- Investigate a new concept for improving the thermoelectric figure of merit of III-V semiconductor thin films, namely the use of quantum dot superlattices to enhance the Seebeck coefficient and reduce the cross-plane thermal conductivity.
- Synthesize and characterize new III-V thermoelectric materials with a high figure of merit.
- Develop and test 3ω thermal conductivity measurement technique (currently unavailable at NREL) for determining the thermoelectric properties of anisotropic thin films will be developed and tested.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc):

   - Designed and laid out a photolithography mask set for the fabrication of the device structures that will be used to measure the cross-plane thermal conductivity, Seebeck coefficient, and electrical conductivity of the QD- superlattices.

   - Performed calibration growth runs of InGaAs SK islands and Se-doped GaAs to determine suitable conditions for forming a high density of InGaAs islands and to determine n-type doping behavior.

   - Began developing the Labview program for controlling the experiment and collecting data.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

3. **Resources:** (facilities, staff, equipment, funding, etc.)

   - Purchased GPIB, DAC boards and electronic components needed for constructing the 3-omega and Seebeck measurement circuits.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

- Thermoelectric solid-state energy conversion devices for cooling and power generation currently use bulk semiconductor alloys as the thermoelectric material. NREL attempts to fabricate and characterize nanostructured III-V thin films based on quantum dot superlattices (QD-SL), which are expected to have a greatly improved thermoelectric performance over their bulk constituents.

- This work should lead to several scientific publications and form the basis for a new materials science research area at NREL.

Proposed Next Steps:

- Work out the processing steps to fabricate the device structures required for thermoelectric characterization. Includes insulator and metal deposition recipes and insulator etching behavior.

- Construct and test the 3-omega and Seebeck coefficient measurement setup.

- Grow and characterize the structure of multilayer QD samples.

Project Title:	**Single Molecule Fluorescence Detection and Imaging**
Principal Investigator:	**Steve Smith, Garry Rumbles**
Performance period:	03/03 - 02/05
Award:	$240,600
Status:	In progress

Goals:

- Establish NREL capability.
- Develop instrumentation and methodology to study single molecule fluorescence, Förster resonant energy transfer (FRET) between isolated fluorophores and a polymer host, and apply these methods to the study of conjugated polymers.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

    - The modified 6-month milestones of the project were met.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.): none

3. **Resources:** (facilities, staff, equipment, funding, etc.)

    - A post-doctoral candidate with specific experience in the subject area of this project was identified and hired.

    - Necessary lab space and specialized equipment needs were identified and procured.

    - Peng Zhang, PhD,-Physical Chemistry (University of Toronto) was hired to share experience in Single Molecule methods applied to chemical reactions monitored at the single-molecule level, design of Fluorescence Resonant Energy Transfer (FRET) based molecular beacons for genetic assays, scanning probe methods applied to the study of single enzymes on surfaces.

4. **Collaborations:** (partnerships, sub-contracts, etc.)

    - A collaboration with staff in the Bio-Energy Center was established to pursue common interests in the area of single-molecule detection and imaging.

Impact/Significance:

The project aims to use the fluorescence of single molecules as an ultra-sensitive probe of exciton energetics and dynamics in conjugated polymers and organic-inorganic composite particles. Using the spatial, temporal and statistical properties of single-molecule fluorescence events, information regarding structure, dynamics and chemical environment of the fluorophore can be gathered. This information will be invaluable in understanding the operation and limitations of current and future polymer-based opto-electronic devices.

Proposed Next Steps:

Initial set-up and experiments with preparing samples of dilute, robust fluorophores.

Project Title: **Lateral Epitaxial Overgrowth of Highly Mismatched Semiconductors**

Principal Investigator: **Mowafak Al-Jassim**
Performance period: 01/01 – 12/02
Award: $220,000
Status: Completed

Goals:

Determine whether epitaxial overgrowth can effectively reduce the defect density in highly mismatched, arsenide and phosphide semiconductor structures to achieve material with good minority-carrier properties as required for the next generation of high-efficiency multijunction solar cells and thermophotovoltaic devices.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - Special templates and procedures were developed for the growth of mismatched III-V layers.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

   - Lateral epitaxial overgrowth of InP and GaP on (001) GaAs by metal-organic vapor phase epitaxy; A. G. Norman, M. C. Hanna, M. J. Romero, K. M. Jones, and M. M. Al-Jassim. Accepted for publication, Appl. Phys. Lett.

   - Characterization of MOCVD lateral epitaxial overgrown III-V semiconductor layers on GaAs substrates; A G Norman, M C Hanna, M J Romero, K M Jones, and M M Al-Jassim, Invited paper presented at ISCS2003, San Diego CA, Aug. 2003.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

4. **Collaborations:** (partnerships, sub-contracts, CRADA, WFO, etc.)

Impact / Significance:

The project demonstrated the viability of lateral epitaxial overgrowth as a means of controlling structural defects in highly mismatched semiconductor structures. We conclude that it can be successfully used for defect engineering in devices based on such structures.

Proposed Next Steps:

We plan to use some of the templates developed in this project to design and fabricate high efficiency III-V solar cells on inexpensive Si substrates. Further, if funding for solid state lighting should be available, these templates will be used to fabricate high brightness, blue light emitting diodes.

Project Title: **Development of a Scalable Hot Wire Technique for the Production of Carbon Single-Wall Nanotubes**

Principal Investigators: **Anne Dillon, Jeff Alleman, Harv Mahan**
Performance period: 10/01 - 09/04
Award: $500,000
Status: In progress

Goals:

- Demonstrate successful single-wall nanotube production with a scalable technology.
- Demonstrate optimization of the hot-wire process for single-wall nanotube production.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

    - The hot wire feed through is currently being constructed in the machine shop.
    - The patent application, PCT/01-19 "Hot Wire Production of Single-Wall Carbon Nanotubes" has been filed. It is now possible to publish the initial demonstration of the production of single-wall carbon nanotubes with hot wire chemical vapor deposition (CVD).
    - The Raman spectrum of the initial HW material between 100-350 cm^{-1} was carefully examined.
    - Statistical analyses on spectra with large data acquisition times is being performed to determine if the narrowing is statistically significant. If it is, the article will be submitted to *Applied Physics Letters*.
    - Optimal catalyst incorporation methods, optimal synthesis temperatures, pressures and gas flow conditions have been explored.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

    - A paper for either *Applied Physics Letters* or *Chemical Physics Letter*s is in preparation. It suggests that the tubes are observed to be isolated.

- Statistical analysis on Raman spectra of the RBMs of both isolated HW and bundled CVD nanotubes has been performed. This final detailed analysis did not reveal that the narrowing observed for the isolated SWNTs was statistically significant. However, since it was possible to make such theoretical/experimental comparison, a manuscript was submitted to *Applied Physics Letters* and comments are soon expected.

- "Hot Wire Production of Isolated Carbon Single-wall Nanotubes" paper has been submitted to *Applied Physics Letters*. The referee accepted it with minor revisions. Revisions have been completed and the manuscript was successfully resubmitted.

- A conference proceedings on the HW-CVD synthesis of SWNTs for the 2nd International Conference on Cat-CVD (Hot-Wire CVD) Process are in preparation.

- An oral presentation is scheduled at the 2nd International Conference on Cat-CVD (Hot-Wire CVD) Process Sept. 10-13, 2003, Denver, CO.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

- All of the equipment has been ordered and received. The chamber and gas manifold have been completely assembled. The necessary new power installation has been performed.

- The construction of the HW chamber including installation of the complex feed through has been finished. The gas handling lines have been completely assembled. An evaporation boat for the introduction of gas phase organo-metallic compounds has been incorporated inside the HW apparatus, and an additional feed through has been connected.

- The appropriate safety precautions for utilizing flammable gases such as hydrogen and methane have been mapped out and incorporated in to the HW set up.

- The readiness verification has been completed, and experiments are in progress.

4. **Collaborations:** (partnerships, sub-contracts, etc.)

Impact/Significance:

- Carbon single-wall nanotubes (SWNTs) have a variety of unique electronic, optical, and mechanical properties making them promising candidates for a wide scope of applications including gas storage and separations, fuel cell membranes, batteries, photovoltaics, composite materials, nanoscale wires, and interconnects. However, for any of these applications to be ultimately realized, it is essential to develop an economical and scalable synthesis technique for the production of defect-free SWNTs at high yield, which may be easily purified. Such a method is not currently available. NREL researchers have demonstrated a "proof of concept" for a hot-wire technique for the production of SWNTs. The researchers have high expectations for the optimization of this novel technique since it is a continuous rather than a batch process, utilizes a gas phase catalyst and should be economically scalable.

Proposed Next Steps:

- Optimize the system parameters.

- Determine the optimal method for catalyst introduction.

- Prepare a paper on synthesis parameters for the favorable production of either MWNTs or SWNTs.

- Establish a routine process for the production of materials with high SWNT densities.

- Enable performance of studies of the production dynamics of bundled versus isolated tubes as well as studies for the production of specific sizes and types of SWNTs.

- Explore purification methods.

Project Title: **Polymer Based Photovoltaic Devices**

Principal Investigator: **David Ginley**
Performance period: 01/01 – 09/03
Award: $500,000
Status: Completed

Goals:

Recent work, especially in the OLED field, has shown that polymer-based heterojunction devices have the potential to become important in future generations of PV and high-efficiency lighting technologies. Organic semiconductors have evolved into a commercially viable technology, with several flat panel displays now on the market from large companies like Kodak, Sony, and Philips as well as numerous start-ups such as eMagin. With the apparent success of this application, many research groups and companies have put increased emphasis on organic based photovoltaics and solid state lighting. U.S. companies such as General Electric and General Atomics, as well as overseas companies such as Siemans and Toshiba, have invested substantially in developing these technologies. Numerous start-ups have arisen recently, including Nanosolar, Nanosys, and Konarka Technologies. Organic semiconductors offer the potential of lower cost, processing ease and compatibility with a variety of other systems. At the start of this DDRD, NREL did not have a program in this rapidly burgeoning area. It was critical that NREL investigate this potentially important new direction for photovoltaics. Based on the current work of the team members, NREL has gotten up to speed rapidly and made significant contributions to this area. They have developed a nationally recognized competency in composite based devices.

Although the project focuses on developing a fundamental understanding of multilayered polymer hybrid optoelectronic devices, the overall goal is to use this knowledge to design and manufacture environmentally favorable, highly efficient, easily processable, and inexpensive polymer-based PV and light-emitting diodes for the next generation of displays, indoor lighting, and renewable energyproduction. A key element of this project was to develop a core competence in this area of polymeropto-electronics and extend this to developing next generation device concepts and to develop new funding and new partnerships internal and external to NREL.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

    - Inert atmosphere based device processing and packaging to remove the effects of oxygen on initial device characterization. This meant configuring a dry box specifically for this project, acquiring an additional box, developing a transportable cell for sample characterization.

    - Development of work-function measurement capability to characterize the effects of surface processing, surface states and interfacial contact.

    - Development of optical characterization tools for absorption and photoemission.

    - Development of device characterization tools for transport and rough efficiency measurement.

    - Development of mask sets and processing for characterization of the electro-optical properties of polymers and small molecules.

    - Establishment of plasma etching and SiOx deposition capabilities.

    - Establishment of a database of organic PV and OLED related materials and references.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

3. **Resources:** (facilities, staff, equipment, funding, etc.)

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

- NREL has developed a state of the art program in organic opto-electronics, which has developed a core competency in organic photovoltaics and is developing a comparable competency in OLEDs for indoor lighting.
- A new class of nano-materials has been made and appears enabling for next generation composite organic photovoltaic cells.
- An robust understanding of the key elements and limitations of organic photovoltaic cells has been developed as well as initial models of device performance. This understanding is key for future device development.
- NREL has developed an acknowledged position in the field as evidenced from the number of invited talks, papers and collaborative agreements.
- Infrastructure is now in place sufficient to continue a state of the art program in organic opto-electronics.
- NREL has begun to develop a viable IP position in this area.

Proposed Next Steps:

Key elements of current laboratory strategic initiatives include the development of a program to look at next generation “over the horizon” photovoltaics in the National Center for Photovoltaics and the initiation of activities to meet the emerging national program on high efficiency lighting. In both cases organic devices offer great potential. In the case of photovoltaic devices this is based on the ability to produce large area devices from low cost materials with atmospheric processing. In the case of OLED based devices there is the potential for large area smart blue or white emitters to be used directly with additional phosphors. In either case, this program has boot-strapped NREL from not having any polymer based photovoltaic or OLED program to having a program that is internationally recognized with a diverse set of collaborators.

The initial OPV program has led to a follow on in the areas of OLEDs. We hope to be able to get support from the PV program. We have initiated a number of CRADAs and proposals to get new funding into this area. We would like to keep the momentum initially established in the DDRD to lead NREL to a position of prominence in this growing area and to fully explore the potential of organic photovoltaic cells.

Project Title:	**Solid-State Nano-composite Materials for Supercapacitor Applications**
Principal Investigator:	**Se-Hee Lee**
Performance period:	03/03 – 02/05
Award:	$240,000
Status:	In progress

Goals:

- Pursue a novel concept that places NREL at the forefront of solid state science and technology in the field of energy storage.
- Synthesize a composite electrode with appropriately sized polycrystalline transition metal oxide nano-particles surrounded by an amorphous solid-state proton electrolyte. In this configuration, nano-particles of transition metal oxide create a high specific capacitance (due to their large surface area) and intimately contact the surrounding solid-state proton electrolyte. This fills in the pores between the nano-particles and maximizes the usage and accessibility of the total particle surface.
- Develop new class of solid-state supercapacitor based on a novel nano-composite structure.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

- Thin films of the Ni-Ta oxide nano-composite were deposited by reactive RF-magnetron sputtering in O_2 from a composite target comprising pie-shaped wedges of Ta metal arrayed radially on circular Ni targets. The thin films were prepared on indium tin oxide (ITO) coated glass for electrochemical and optical transmittance measurements and on polished stainless steel substrates for Raman spectroscopy. The average thickness of the films was 200 nm. NiO and Ta_2O_5 films were also deposited by reactive RF-magnetron sputtering from metal Ni and Ta targets, respectively. Electrochemical behavior of the Ni-Ta oxide nano-composite electrodes was examined using cyclic voltammetry (CV) in either 3M KCl or 1M KOH electrolyte solution.

- CV curves of the as-deposited Ni-Ta oxide nano-composite electrodes in 3M KCl at a voltage scan rate of 10 mV/s indicate capacitive behavior. This composite NiO-Ta_2O_5 material exhibits electrochemical capacitance of 157 mF/g. Compared to the NiO film electrode, the CV curve of the Ni-Ta nano-composite electrode is more rectangular shape indicating its capacitive behavior.

- Two different structural features were observed in nano-composite of NiO and Ta_2O_5 deposited by reactive RF-magnetron co-sputtering from Ni/Ta metal composite target —

pure tantalum oxide and nickel oxide nano-particles embedded in tantalum oxide (confirmed by energy dispersive spectroscopy analyses). Selected-area electron diffraction (SAED) patterns and bright-field images of the P1 and P2 regions revealed an interesting discovery. The presence of a weak and wide ring in the SAED pattern for the pure tantalum oxide region is evidence for an amorphous nature of tantalum oxide which is in agreement with a high resolution bright-field image of this same region. In contrast, the SAED pattern for the nickel oxide nano-particles embedded in tantalum oxide region indicates well-crystallized particles. The bright-field image for the first region indicates that the size of these nickel oxide particles ranges from 5 to 10 nm. This unique nano-composite mixture (of polycrystalline nano-particles of nickel oxide and intimately surrounding an amorphous tantalum oxide electrolyte) constitutes an ideal structure with great potential for fabricating improved solid-state supercapacitors.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

3. **Resources:** (facilities, staff, equipment, funding, etc.)

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

Proposed Next Steps:

- The structural and compositional properties of the Ni-Ta oxide nano-composite films will be optimized by varying the RF sputtering power and the working pressure.
- The compositional ratio of the composite will be adjusted by changing the surface ratio of the tantalum arrayed nickel target.
- Raman spectroscopy, TEM, and AC impedance spectroscopic analyses will be used to evaluate the micro-structural and interfacial characteristics of these nano-composite electrodes.

Advanced Measurement and Characterization Techniques

Project Title: **Tunneling Spectroscopy Studies of the Effect of Adsorbates on the Electronic Structure of Semiconductor Nanoparticles**

Principal Investigator: **Art Frank**
Performance period: 06/01 – 05/03
Award: $250,000
Status: Completed

Goals:

Provide new and important insight in understanding surface properties (e.g., surface states) and phenomena associated with surface states (e.g., light-harvesting, electron transport and recombination) of nanocrystals that constitute the building blocks of a new type of solar cell based on dye-sensitized nanocystalline TiO_2 films.

Accomplishments:

1. **Technical:**

2. **Visibility:** (proposals, presentations, publications, conferences, etc)

- Submitted a proposal based, in part, on this DDRD project, entitled “Electronic Communication in DNA-Engineered Nanoscale Materials” to the Office of Science in January FY02 in response to their call for proposals under the Nanoscale Science, Engineering, and Technology Initiative. The value of this proposal is $2.5M over the initial four years. To our knowledge, only Office of Science nanoscience centers were funded in this initiative. However, we were invited to resubmit this proposal in FY03.

- In April FY03, Jao van de Lagemaat participated in a response to the Office of Science’s call for a proposal under their catalysis initiative. The submitted proposal, entitled “Exploring Light-Driven Bioinorganic Catalysis: Synergy between Molecular and Enzymatic Processes Bound to Nanotube Surfaces”, is concerned, in part, with the electronic interaction of TiO_2 nanoparticles with molecular adsorbents. This proposal, which is for $2.4M over the initial three years, in under review.

- A related DDRD project entitled “Electronic Communication in Assemblies of Semiconductor Nanoparticles” by two of the team members was funded for $300K for two years starting May FY03. This project is concerned with the electronic properties of single quantized nanoparticles and their relation to electrical conduction in nanoparticle arrays.

- J. van de Lagemaat, H. Mountinho and Artur J. Frank, “AFM and STM Studies of Monolayers of Ultrasmall Anatase TiO_2 Nanoparticles”, Abstracts of the 203rd Meeting of the Electrochemical Society, Paris, France, Abstract # 2737.

- A manuscript of the work under the DDRD project is being prepared for a peer review journal.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

The results demonstrated the feasibility of preparing organized monolayer assemblages of monodispersed ultrasmall TiO2 nanoparticles and of studying them by techniques that are sensitive to probing the electronic structure of a single nanoparticle. The capability to organize nanoparticles in two-and three- dimensional structures is a major goal in nanoscience in general and in nanoparticle-based solar cells in particular.

Proposed Next Steps:

The technology developed to create two-dimensional arrays of nanoparticles will be valuable in an upcoming project on the electronic communication in quantum dot arrays.

Project Title: **Single-Crystal X-ray Diffraction Facility (Capability)**

Principal Investigator: **Philip Parilla**
Performance period: 08/02 – 12/04
Award: $130,000
Status: In progress

Goals:

Establish NREL capability to perform X-ray diffraction measurements and analyses on single crystals, a fundamental analytical tool to ascertain crystalline structure in new materials.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

   - Denver X-ray Conference and several tutorials on x-ray diffraction were attended to help develop skills and improve knowledge.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

- The equipment needed to supply the cooling water has been installed and is operational.
- The safety enclosures have been set up and the interlock system has been reconnected and appears to be operational.
- The electrical power for the generators has been connected and is operational.
- Laboratory fit-up was completed in late February 2003.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

X-ray diffraction is the primary technique used to ascertain crystalline structure in materials, and thus it is a fundamental analytical tool. In this project, researchers are establishing the capability at NREL to measure and analyze X-ray diffraction of single crystals. By establishing a set-up and core competencies in single-crystal X-ray diffraction, and analysis of data, this project will enhance NREL's ability to investigate and understand new material systems as they apply toward scientific and technological questions.

Proposed Next Steps:

Prepare the x-ray generators for readiness verification and certification.

Project Title: **Construction and Validation of Automated Sequential Air Samplers for use in Building Sampling Applications**

Principal Investigator: **Ed Wolfrum**
Performance period: 04/02 – 10/02
Award: $62,000
Status: Completed

Goals:

- To develop methods and techniques for unattended air sampling of building spaces and rapid interpretation of the results.
- Construct five automated ambient air-sampling units and validate their operation.
- Collect ambient air sampling from different building spaces at NREL.
- Perform chemometric analysis of the collected data.
- Determine whether "chemical fingerprints" of the different building spaces could be identified.

Accomplishments:

1. Technical: (scientific, IP creation, etc.)

- Developed methods and techniques for unattended air sampling of building spaces and rapid interpretation of the results.
- Constructed five automated ambient air-sampling units and validate their operation.
- Collected ambient air sampling from different building spaces at NREL.
- Performed chemometric analysis of the collected data.
- Identified "chemical fingerprints" of the different building spaces.

2. Visibility: (proposals, presentations, publications, conferences, etc.)

3. Resources: (facilities, staff, equipment, funding, etc.)

4. Collaborations: (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

We clearly demonstrated that, by performing chemometric analyses on ambient air samples, it is possible to classify different spaces in a single building, thus providing a "partial fingerprint" of air quality in indoor spaces. This could provide a valuable tool for diagnostics and source identification in indoor air quality monitoring.

Proposed Next Steps:

The future plans are to secure funding to perform systematic sampling and analysis of many different indoor spaces at NREL, to clearly show the utility of the chemometric approach to begin to quantify indoor air quality.

Bioenergy, Biotechnology, Chemistry

Project Title: **Nitrogen Conversion to NOx in Biomass Thermochemical Processes**

Principal Investigator: **David Dayton**
Performance period: 06/02 – 06/05
Award: $406,907
Status: In progress

Goals:

Develop a fundamental understanding of the forms of nitrogen in biomass, and insights into the mechanism and kinetics of how fuel-bound nitrogen transforms to NOx in biomass thermochemical conversion processes.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - Task 3. Biomass Combustion Experiments
     The labeled alfalfa has been received and is being prepared. Samples were separated and milled for experimental use. Preliminary pyrolysis and combustion experiments with labeled and unlabeled material is planned for next quarter.

   - Task 4. Biomass/Coal Cofiring Experiments
     No planned activity until Year 3.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

3. **Resources:** (facilities, staff, equipment, funding, etc.)

   - Stephen Ogle, at CSU/NREL has taken over the daily responsibility for this project.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

   - Task 1. Growth of Isotopically-Labeled Biomass:

   Two varieties of witch grass seeds were obtained - Blackwell (seed lot SWB-3200) and Alamo (SWA-1154). Half were sent to CSU and half were kept at NREL.

   Dr. Johan Six is the PI for a subcontract with the Natural Resources Ecology Lab at the Colorado State University to complete this three-year subcontract. First alfalfa plants are expected to be harvested by the end of 02/2003. Six, who still has part of his time covered by CSU, makes periodic trips back to CSU to oversee this project.

   Also in support of this task NREL has been developing its own capabilities in growing labeled biomass materials but on a much smaller scale. Selected corn samples were planted and watered/fertilized, four of them labeled and four unlabeled (controls), and grown in the FTLB greenhouse. The plants were harvested and are now being dried.

- Task 2. ^{15}N CPMAS NMR Experiments:

^{15}N-labeled algal lyophilized cells, obtained from Cambridge Isotope Laboratories, were purchased and used as a surrogate until the ^{15}N-labeled plants are harvested. The cells are being used to optimize experimental parameters and to test new ideas. ^{15}N solid-state nuclear magnetic resonance (NMR spectra) spectra have been collected on ^{15}N-labeled cells. The NMR analysis is able to distinguish five different nitrogen forms. We are growing ^{15}N labeled corn in the NREL greenhouse, in conjunction with the work being performed at CSU, in order to learn how to label plants for future studies. The corn is being grown under the same conditions as CSU, however, we are having trouble establishing the plants and they are not growing too well. We are attempting to grow three different corn varieties with different cell wall chemistry for analysis.

Impact/Significance:

Proposed Next Steps:

- Task 1. Growth of Isotopically-Labeled Biomass:

  - The alfalfa and the Blackwell variety of the switch grass were successfully established and are regularly watered with ^{15}N labeled Hoogaland solution. The watering will be continued until harvest. The alfalfa plants were harvested in 3/03 and samples of plants and roots are being separated and prepared. Plant material is being oven dried and ground. Alfalfa samples were delivered to NREL in 6/03. Samples were milled in preparation for experimental work.

  - Labeled switch grass is still growing and will be harvested when plants are large enough to provide the amount of material expressed as a deliverable. Short winter days limited the growth of the switch grass plants. The longer days of spring are improving the growth rate of the switch grass.

- Task 2. ^{15}N CPMAS NMR Experiments:
- Begin NMR experiments with labeled alfalfa that has been obtained.

- Task 3. Biomass Combustion Experiments:
- Combustion and pyrolysis experiments will be performed with the algal lyophilized cells to investigate how ^{15}N labeling impacts the mass spectrometry results. Preliminary pyrolysis and combustion experiments with the labeled and unlabeled alfalfa received will begin next quarter.

- Task 4. Biomass/Coal Cofiring Experiments:
- No planned activity until year three.

Project Title: **Development of Stable Catalysts for the Electrochemical Reduction of CO_2 to CO**

Principal Investigator: **Dan DuBois**
Performance period: 10/01 – 09/03
Award: $215,503
Status: In progress

Goals:

- Develop stable catalysts for electrochemical reduction of CO_2 to CO
- Promote NREL's leadership role within the scientific community in the area of carbon dioxide utilization
- Pursue designed approaches for improving electrocatalysts for CO_2 reduction
- Develop interactions with the University of Colorado that would be useful in the future for developing an NREL center for CO_2 utilization.
- Demonstrate increased catalyst turnover numbers (catalyst stability) by incorporation into thin films of ionic liquids, and by synthesis of a designed catalyst expected to combine high rates and stability.
- Establish interactions with the University of Colorado in CO_2 chemistry.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - Selected ionic liquids and the most stable catalyst studied previously have been synthesized.

   - A new ligand designed to promote catalyst stability has been prepared. Ultimate turnover numbers for this catalyst should be much larger than those of any previous catalyst studied for this class of catalysts. Mechanistic studies of these catalysts have also been completed.

   - Preliminary studies with thin films indicated that coating edge pyrolytic graphite electrodes with thin films could produce thin films in which electroactive molecules such as ferrocene could be easily observed.

   - CO_2 reduction catalysts were incorporated into these films, but results have not been reproduced. A number of possible factors for this irreproducibility were examined. Most recent results indicate that this instability appears to be largely mechanical.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

   - Interactions with the University of Colorado are in place. The PI of this project participated in writing a proposal with Professors Rich Noble and Mary Rakowski DuBois from the Departments of Chemistry and Chemical Engineering that has been funded by NSF. This result has strengthened interactions between CU and NREL in this area.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

- Jim Raebiger was hired as a postdoctoral researcher, and he will be working half time on this project. Jim received his Ph.D. from Harvard and did a previous postdoc at the University of Utah.

4. **Collaborations:** (partnerships, sub-contracts, etc.): none

Impact/Significance:

Proposed Next Steps:

- The instability of the thin films was unexpected based on literature precedent. However, now that it is known that the lack of reproducibility is caused by mechanical instability, the first objective will be to simply avoid physical contact with the thin films by redesigning the electrochemical cells.

- A second, longer-term strategy is to try to stabilize these films by the addition of polymers such as Nafion or other surface modification so that the interaction between the thin film and the electrode surface is stronger.

Project Title: **Realizing Biorefineries: Expanding the Sugars Platform Using New Biomass-Derived Sugar Products**

Principal Investigators: **Jim McMillan, Rick Elander, and Kelly Ibsen**
Performance period: 07/00 – 07/03
Award: $490,000
Status: Completed

Goals:

- Further develop the bio-refinery concept
- Identify opportunities to use lingocellulosic biomass to expand the existing industrial sugars platform to include D-xylose based products

Accomplishments:

1. **Technical (scientific, IP creation, etc).**

- Market Assessment (Task 1a). An analysis of world sugar markets was completed.

- Process Engineering and Economic Analysis (Tasks 1b and 1d). Extensive analysis was performed to identify cost-effective methods of producing xylose syrups of various purities as a co-product of a biomass to ethanol facility. The approach was to explore processes for producing syrups comparable to existing glucose syrups, i.e., containing approximately 70% solids and approximately 95% dextrose equivalents.

- Refine Technoeconomic Modeling (Task 2a). In FY03, the earlier process engineering models developed for producing xylose-rich sugar syrup products were refined to increase the rigor of both the models and the subsequent economic analyses used to estimate MXSP values. Work to reduce to practice aspects of the novel separations concept developed in the project was also pursued during Task 2.

- Record of Invention 02-33 (McMillan, 2002).

2. Visibility (proposals, presentations, publications, conferences, etc)

- Neeves, K.B.; McMillan J.D.; Sinor, J.; Elander, R.; Ibsen, K. 2000. Sugar Market Analysis. NREL Internal Milestone Report (10/30/2000), Biomass Program Valuable Documents Database, Document Number 4998.

- Neeves, K.B. 2001a. Review of Membrane Filtration Opportunities for Sugar Solution Purification and Concentration. NREL Internal Technical Memo (02/09/2001), Biomass Program Valuable Documents Database, Document Number 5151.

- Neeves, K. 2001b. Review of Preparative Chromatography Methods for Multicomponent Sugar Separation. NREL Internal Technical Memo (02/20/2001), Biomass Program Valuable Documents Database, Document Number 5186.

- Neeves, K.B.; McMillan J.D; Elander, R.T., Ibsen, K.; Jechura, J. "Expanding the Biomass Sugar Platform: An Investigation of Sugar Separation and Purification Techniques." Oral paper (presented by K. Neeves) at the 23rd Symposium on Biotechnology for Fuels and Chemicals, May 6-9, 2001, Breckenridge, CO.

- Neeves, K.B.; McMillan J.D. Task 1b. "Process Engineering and Technoeconomic Analysis." NREL Internal Milestone Report (06/03/2001), Biomass Program Valuable Documents Database, Document Number 5597.

- Albertus, P. "Realizing Biorefineries by Expanding the Sugars Platform: Monosaccharide Separation." Unpublished paper and PowerPoint presentation (delivered 08/10/2001 as part of DOE's Energy Research Undergraduate Laboratory Fellowship Program; PA was a University of Michigan, Ann Arbor, ChE student who interned at NREL under the ERULF program.) Posted in the Project's restricted Y: drive folder.

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- Scarlata, C. "Xylose Review, Part I: Solvents and Polyols. Draft manuscript." (03/13/2003) for future submission to peer-reviewed journal (still needs introduction and conclusions). Posted in the Project's restricted Y: drive folder.

- Jechura, J. "Techno-Economic Assessment of Xylose Separation Sub-Processes Within a Biomass-to-Ethanol Plant." NREL Internal Technical Memo (6/25/2003). Posted in the Project's restricted Y: drive folder.

- Scarlata, C. "Novel Sugar Separations Experimental Details." NREL Internal Technical Memo (8/7/2003). Posted in the Project's restricted Y: drive folder.

3. **Resources** (facilities, staff, equipment, funding, etc)

4. **Collaborations** (partnerships, sub-contracts, CRADAs, WFOs, etc)

    - A collaboration with Amalgamated Research, Inc. (Jechura and McMillan, 2003).

Impact/Significance:

- An analysis of world sugar markets showed that carbohydrate prices are continuing to steadily erode. The implication is that it will be very difficult for sugars derived from lignocellulosic biomass to compete head-to-head with very inexpensive starch-based glucose syrups in commodity sugar markets. While production of industrial chemicals from D-xylose potentially can become economically attractive if D-xylose sugar products can be priced competitively at approximately 3-8¢/lb sugar, this is considered at best a longer term prospect likely to require substantial additional technology development to realize. In the shorter term, the major opportunities appear to be in finding cost-effective methods to produce moderate volumes of xylose-rich sugar products that will command a modestly higher value than current sugar products because of xylose's relatively unique pentose (five carbon sugar) nature relative to other widely available hexose-based carbohydrates.

- Preliminary work initiated in FY01 examined a variety of potential methods of upgrading a xylose-rich hemicellulose hydrolysate process stream (which presumably would be available as a slipstream from a biomass to ethanol facility) into lower purity mixed sugar or higher purity xylose-rich syrup products. Ultimately, out of several potential processing schemes investigated, more detailed economic modeling on a process for upgrading hemicellulosic sugar-rich biomass hydrolysates were selected and performed. This first phase of process engineering and techno-economic modeling calculations estimated that xylose-rich mixed biomass sugar syrup could be produced for a minimum xylose selling price (MXSP) of roughly $0.20/lb xylose, whereas higher purity xylose syrup could be produced for an MXSP of about \$0.45/lb xylose. These selling prices were essentially independent of sugar syrup concentration over the range of 100 – 700 g/L.

- The estimated minimum selling prices for xylose-rich sugar products are well below prices for reagent grade xylose, but are much too high for such syrups to effectively compete in existing (hexose-based) global sugar markets. This initial outcome resulted in modifying the original plan by extending Tasks 1b and 1d to further develop chromatography modeling tools, exploring alternative approaches to hemicellulose hydrolyzate upgrading with the potential to decrease the cost of producing xylose syrups, especially high purity xylose syrups. Also, work was redirected on products from xylose (Task 1c) to focus on higher-value products for which the higher estimated MXSP would be less of an impediment.

- Additional work on modeling chromatographic separation of mixed biomass sugars was completed early in the Task 1b extension. Although substantial progress was being made in this area, efforts were transitioned to examining an innovative approach for separating sugars that would exploit the substrate specificity of sugar-utilizing microorganisms which could possibly greatly decrease sugar-sugar separation costs. Tasks 1b and 1d were thus extended to explore the cost reduction potential of a novel separations method for upgrading xylose-rich hemicellulose hydrolyzates. This idea is the subject of NREL Record of Invention 02-33 (McMillan, 2002). Preliminary economic modeling completed in FY02 showed that this novel separations approach can potentially reduce the cost of producing a higher-purity xylose syrup from about \$0.45/lb to \$0.25-0.35/lb. Based on these results, NREL's DDRD program management approved refocusing Task 2 work on refining the techno-economic modeling of this novel separations concept and trying to reduce to practice this method of biomass sugar purification.

- The highlight findings of the Task 2 analysis work were technoeconomic projections that suggested that much higher purity xylose products could be produced for only slightly higher cost (\$0.16-\$0.20/lb xylose) than lower purity xylose products by incorporating the newly proposed novel separations approach.

- Work to reduce to practice aspects of the novel separations concept was also pursued during Task 2. Results of preliminary experiments show that the proposed approach is technically feasible. Furthermore, examples developed during this phase of the work vividly demonstrate that the proposed separations innovation can be used to achieve any of a wide number of sugar purifications, thus providing a powerful, lower cost method for purifying targeted sugar(s) in mixed sugar solutions than traditional methods based on chromatography. While only a limited number of experiments were completed in Task 2 to demonstrate "proof of concept," there are almost limitless possibilities of how this general approach can be applied to improve the economics of separating/purifying/recovering a wide variety of target molecules from complex mixtures.

Proposed Next Steps:

- Continue to pursue leading edge biorefinery-related ideas within the DDRD program, since this program has considerably more flexibility than DOE's more structured Biomass RD&D Program. Researching along multiple alternative paths is essential to build the NBC's critical depth and breadth in this area as well as to spur commercialization of lignocellulose sugar platform-based biorefineries.
- Promote increased depth, breadth of savvy, and interest within NBC personnel for R&D on biorefinery-related separations.
- Seek opportunities to further develop: a) chromatographic modeling and related experimental capabilities; and b) novel separations concepts that can be applied to bioconversion process streams.

Project Title: **Computational and Experimental Kinetic Studies of Biomass Pyrolysis Components**

Principal Investigator: **Mark Nimlos**
Performance period: 01/01 – 12/03
Award: 350,000
Status: In process

Goals:

- Develop computational and experimental techniques for understanding and improving biomass thermochemical processes.
- Model reactive flow mixtures in a micro-reactor that has been used for qualitative analysis of thermal reactions and extract quantitative kinetic data for reactions of importance in the thermal treatment of biomass.
- Develop computational capabilities for modeling reactive flow mixtures
- Develop micro-reactor for kinetic measurements.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - Additional experiments of the thermal degradation of allyl ethyl ether to acetaldehyde and propene in the hyperthermal nozzle were conducted. These recent experiments will help determine the experimental uncertainty of the residence times and temperatures.

   - Thermal decomposition of diethoxy methane (a model compound containing an acetal group) has been measured using time-of-flight (TOF) mass spectrometry and matrix isolation infrared spectroscopy.

   - Experiments conducted with a goal of studying the thermal decomposition of gallium compounds. These experiments may help understand important chemical reactions in the formation of thin film photovoltaic devices using metal organic chemical vapor deposition (MOCVD).

   - *A*dditional experiments of the thermal decomposition of laevoglucosan (an important intermediate in the pyrolysis of cellulose) have been conducted. Results need to be analyzed.

2. **Visibility:** (proposals, presentations, publications, conferences, etc): none

3. **Resources:** (facilities, staff, equipment, funding, etc): none

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.): none

Impact/Significance:

- Biomass thermochemical conversion technologies are being developed to convert biomass to electricity, fuels, and chemicals via three main pathways: pyrolysis, gasification, and combustion. Collecting detailed quantitative information is a crucial step toward the commercialization of biomass thermochemical conversion technologies. This information can be used to help identify promising pathways and assist in reactor design and scale up.

- This research project will develop a new experimental technique capable of collecting quantitative kinetic information on thermochemical conversion processes far more rapidly than is currently possible.

- Expanding NREL's capabilities in Computational Fluid Dynamic modeling, researchers will apply these computational methods to measure reaction kinetics in a pulsed micro-reactor at time scales much shorter than achievable in other continuous flow reactors.

- This project will begin the process of establishing NREL as a world leader in computational methods and experimental techniques for determining accurate, quantitative kinetics for biomass thermal conversion processes.

- The results will aid in optimizing existing processes and help facilitate the successful scale up and commercialization of developing processes.

Proposed Next Steps:

- Analyze data for allyl ethyl ether and conduct addition experiments as needed.
- Analyze data from diethoxy methane and laevoglucosan.
- Conduct experiments with gallium and boron compounds.

Project Title: **Determining Metabolic Profiles (Metabolomics) of Saccharomyces Cerevisiae Mutants with Nuclear Magnetic Resonance and Molecular Beam Mass Spectroscopy**

Principal Investigator: **Arjun Singh & Mark Davis**
Performance period: 06/03 – 05/05
Award: $380,265
Status: In progress

Goals:

This project addresses the largest problem in the post-genomics era: the ability to rapidly assign a function to sequenced but uncharacterized genes using metabolic profiling and multivariate statistical data analysis.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.):

- A library of yeast gene deletion strains has been identified and is in the process of being purchased.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

   - A proposal was submitted to the Interagency call for metabolic engineering: "Modeling Phenylpropanoid Metabolism and Dynamics in Cultured Populus Cells Via High Throughput Transformation and Chemical Profiling".

3. **Resources:** (facilities, staff, equipment, funding, etc.)

   - A follow-on funding in the amount of $930K for three years has been obtained.

   - Three candidates have been interviewed for the two postdoctoral positions available for this project. An offer has been made to one candidate, R. Vadali, and a second offer will be made shortly to one of the other two candidates.

4. **Collaborations:** (partnerships, sub-contracts, etc): none

Impact / Significance:

- Microorganisms will play a key role in the efficient production of ethanol and other products from biomass. The economic value of biomass will only be realized once the process is inexpensive enough to compete successfully against other sources of energy—fossil fuels or other renewable sources.

- NREL attempts to answer three key questions that exist regardless of the microorganism chosen to produce the desired product. First, can metabolic pathways be identified which are bottlenecks in the production of ethanol or other bioproducts? Secondly, what improvements must be made in the metabolic flux through these identified pathways? Finally, since microorganisms are exposed to harsh environments during biomass utilization, what effect does exposure to a wide variety of compounds and growth conditions have on the cell's metabolism and how are these effects reflected in production yields?

- Genome sequencing and the production of gene maps have far out-stripped the ability to rapidly discover and annotate the function of unknown genes. After a genome is completed, roughly one-third of the genes are identified as similar (by protein sequence only) to known genes in other organisms while an additional third is completely novel. The methods developed with this project will create a new tool for assigning gene function within the metabolic pathways.

- The model yeast organism will be used to validate the metabolomic approach described and to show its utility to identify the function of sequenced but uncharacterized genes.

- Metabolomics is a new field that examines the metabolic state of a cell *in toto* and can be used to determine kinetic flux through pathways as well as the pool size of the metabolites themselves. From this information, a model of the cell's metabolism can be established. This project will develop methods to help answer the three questions posed above with a relatively rapid throughput method.

- In addition, these innovative methods will lay the foundation for additional research as more analytical equipment becomes available, specifically, a Liquid Chromatograph-Mass Spectrometer (LC-MS).

- Finally, the methods developed will be instrumental in quickly determining the metabolic state of a fermentation culture during biomass utilization as well as in the selection of higher production microorganisms.

Proposed Next Steps:

Hire postdocs and begin to determine experimental protocols for yeast fermentations.

Project Title:	**Carbon Allocation and Partitioning in Woody Plants: A Means to Enhance Bioenergy Conversion and Carbon Sequestration**
Principal Investigator:	**Mark Davis**
Performance period:	10/99 – 01/03
Award:	$496,000
Status:	Completed

Goal:

Discover the genetic basis for mechanisms controlling the quantity and quality of photosynthate allocation into secondary cell walls in roots and stems of woody plants as a means of understanding the biological processes that underlie the production and use of biomass for energy.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

    - We successfully established inter-laboratory expertise in Populus genetic mapping as it relates to energy and bio-based feedstock quantity and quality (i.e., carbon allocation and partitioning, respectively) by analyzing a segregating hybrid Populus families and identifying genetic markers linked to these processes. As a proof-of-principle that cell wall chemistry impacts conversion efficiencies, dilute acid hydrolysis of samples with high and low lignin content and/or S/G ratio demonstrated that higher fermentable sugar concentrations can be obtained from samples with lower S/G ratios.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.

    Publications:

    - Davis, M.F.; Tuskan, G.A.; Payne, M.M.; Strauss, S.H.; Tschaplinski, T.J.; Meilan, R. *Assessment of Populus Wood Chemistry Following the Introduction of a Bt Toxin Gene*. In preparation.

    - Davis, M.F.; Dinus, R.; Tuskan, G.A. *A Rapid Method for Measuring Syringyl to Guaiacyl Ratios in Hybrid Poplar*. Submitted to Holforschung.

    - Lagutaris, R.L.; Davis, M.F. *Measuring Syringyl/Guaiacyl Ratios in Hardwood Species by 13C NMR and Thioacidolysis*. Accepted for publication: Journal Wood Chemistry.

New Proposals:

- The collaboration with T. Tschaplinski (above) resulted in the proposal: *Auxin Regulation of Wood Quality in Sweetgum and Loblolly Pine*. (Tschaplinski, T. ORNL, P.I.), submitted to OIT Agenda 2020 Forest Products call for FY 2001.

- The collaboration with J. Tuskan, above, (ORNL and DDRD/LDRD Co P.I.) resulted in the proposal: *Influence of Growth Environment and Silvicultural Practices on Wood Composition and Quality*. (Davis, M.F., P.I., Tuskan, G.A. and Nowak, C. SUNY, co-P.I.s), submitted to OIT Agenda 2020 Forest Products call for FY 2001.

- Busov, V.; Mielan, R.; Davis, M.; Strauss, S. *Functional characterization of the GA2ox gene family in poplar*. Submitted to NSF. Received favorable reviews but was not funded.

- Strauss, S.; Kelley, S.; Davis, M.; Mielan, R.; Gartner, B. *Functional Genomics of Regulatory Genes in Poplar*. Received good reviews but not funded.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

New Funding:

- A proposal submitted to Biological and Environmental Research, Carbon Sequestration Research Program, “Genetic and Environmental Controls of Carbon Sequestration”, by ORNL was funded for three years, $1.2M total. NREL will be a subcontractor and perform analysis of fine root and leaf chemistry.

- A proposal submitted to OIT/Agenda 2020 Forest Product solicitation entitled “Environmental Influences on Populus and Loblolly Pine Wood Chemistry and Density” was funded for four years, $950K total. The PIs are Gerald Tuskan (ORNL) and Mark Davis (NREL). This project was accepted for funding. NREL will receive ~300K over four years.

4. **Collaborations:** (partnerships, sub-contracts, etc.)

- Continuing collaboration with J. Tuskan, ORNL.

- A new collaboration has been started with John Davis and Janice Cooke, University of Florida, to study the effect of nitrogen loading (fertilization) on cell wall chemistry. We have made several presentations and a publication is planned.

- We have agreed to screen a series of transgenic trees for cell wall chemistry changes for Arborgen (Analytical Services Agreement is in place).

- We have developed several collaborations at Oregon State University with Rick Meilan and Victor Busov. Both of these collaborations lead to submission of proposals to NSF.

- We have developed a new collaboration with Andrew Grover at University of California at Davis.

Impact/Significance:

These markers have allowed us to identify regions of the genome that contain genes that control carbon allocation and partitioning in Populus. It appears (1) that carbon allocation (i.e., the distribution of carbon to stems, limbs, roots, etc.) is controlled by a small number of genes, (2) that many of the genes controlling cell wall chemistry (i.e., carbon partitioning) operate independently above- and below-ground, and (3) that genes controlling carbon allocation are independent of genes affecting carbon partitioning.

Proposed Next Steps:

These results are being used to obtain further funding in the areas of carbon management: specifically related to understanding the relationship of the different plant anatomical fractions and soil chemistry. During the course of this project, we were able to partner with K. Magrini (NREL) and P. Payne (Boise Corp) to study the changes in soil carbon related to plantation production of poplar. These results are being used to support a proposal that will be submitted to the Office of Science in FY04.

The analysis methods developed and the cell wall chemistry results obtained during the course of this work have also been used to support several proposals in the area of understanding the relationships between genetic manipulation and the resulting cell wall changes. We expect to continue to work in this area but the decision of the Office of Biomass Programs to not support further work in the area of feedstock development will mean that funding for these efforts will be collaborative projects with University partners.

Project Title: **Validation of the First Lignin Depolymerase**

Principal Investigator: **Michael Himmel**
Performance period: 01/01 – 02/03
Award: $400,000
Status: Completed

Goals:

- Validate a lignin-depolymerizing enzyme having the potential to redefine many biomass-based technologies.
- Obtain data useful for adapting or improving the new enzyme for industrial use.
- In collaboration with the University of Minnesota, expediently achieve two important objectives:
- Purify and suitably characterize a wild-type lignin-degrading enzyme to permit evaluation by industry, and clone the gene coding of this new enzyme into *E. coli* or yeast.
- Establish a physico-chemical lignin characterization capability in the center.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

    - This two-year project began with the intentions of validating new findings from the laboratory of Dr. Simo Sarkanen regarding new lignin degrading enzyme(s) from *T. cingulata*. During the course of the work, it became clear that even with NREL's novel ideas about purification of enzymes contaminated with lignin, achieving the complete removal of lignin from culture proteins was not possible. When these partially purified enzyme samples were subjected to amino acid analysis, the trace phenolics proved to invalidate the results. Thus, neither Sarkanen or NREL group were able to obtain enough possible LD during the first year of the project to obtain amino acid sequence data. This meant that no gene sequence would be forthcoming. In order to maximize the benefit for NREL, we then shifted the project focus to building a unique lignin molecular weight characterization capability at NREL.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

  - A refereed article: "Characterization of Jack Pine Kraft Lignin Using Multi-Angle Laser Light Scattering," *Applied Biochem. and Biotech.* Gidth, A.; Vinzant, T.; Decker, S.R.; Himmel, M.E.; Williford, C. In press.

  - "Proteases and the Extracellular Lignin Depolymerase Activity from *Trametes cingulata",* by Chen, Y.; Vinzant, T.B.; Decker, S.R.; Jennings, E.; Himmel, M.E.; Sarkanen, S. 24th Biotechnology Symposium for Fuels and Chemicals, Gatlinburg, TN May, 2002.

  - "The Effect of Lignin Modifying Enzymes on the Molecular Weight Distribution of Kraft Lignin", by Decker, S.R.; Gidh, A.; Himmel, M.E.; Vinzant, T.B. The 25th Symposium on Biotechnology for Fuels and Chemicals, Breckenridge, CO. May, 2003.

  - "The Effect of Lignin Modifying Enzymes on the Molecular Weight Distribution of Kraft Lignin", by Gidth, A.; Vinzant, T.B.; Decker, S.R.; Himmel, M.E.; Williford, C. To be presented at the AIChE 2003 Annual Meeting, San Francisco, CA, November 16-21, 2003.

  - "Detection of Lignin in Enzyme Mediated Depolymerization Studies by HP-SEC Using Multi-Angle Laser Light Scattering", by Gidth, A.; Vinzant, T.B.; Decker, S.R.; Himmel, M.E. Williford, C. To be presented at the AIChE 2003 Annual Meeting, San Francisco, CA, November 16-21, 2003.

  - "Characterization of Jack Pine Kraft Lignin Using Multi-Angle Laser Light Scattering", by Gidth, A.; Vinzant, T.B.; Decker, S.R.; Himmel, M.E.; Williford, C. To be presented at the AIChE 2003 Annual Meeting, San Francisco, CA, November 16-21, 2003.

  - Proposal: *Catalytic Processing to Convert Lignin Intermediates to Half of U. S. Chemical Needs*, submitted 5/16/03 to the USDA/DOE Biomass R&D Solicitation, entitled", by Meister, Ragauskas, Himmel, and U.S. Plastic Lumber. (NREL asking for $200K per year for three years).

  - Proposal: *Ionic Liquids for Biomass Lignin Processing,* submitted 5/16/03 to the USDA/DOE Biomass R&D Solicitation; entitled", by Ragauskas, Moens, and Decker. (NREL asking for $100K per year for three years).

  - Proposal: *Role of Hemicellulose and Accessory Enzymes in Reducing Pretreatment Severity*, planned for the FY04 AOP, DOE Office of the Biomass Program; entitled". By Decker et al.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

  - Our work on the DDRD funded project attracted a graduate student from the University of Mississippi, Ms. Aarti Gidth, who was able to come to NREL for six months to work with the HPSEC MALLS development.

  - During the course of the two-year project, four NREL staff members were trained in light scattering technology at Wyatt Engineering, in Santa Barbara, CA, including Himmel, Decker, Ding, and Vinzant.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

  - University of Minnesota, Dr. Simo Sarkanen

  - University of Mississippi, Department of Chemical Engineering; Dr. Clint Williford

- Institute of Paper Science and Technology, Dr. Art Ragauskas
- Forest Products Research Center, Dr. John Meister
- Wyatt Engineering, Dr. Michelle Chen

Impact/Significance:

Plant biomass is composed of three primary structural polymers: cellulose, hemicellulose, and lignin. Many industrial processes based on biomass feedstocks would benefit from low cost and environmentally friendly methods for lignin removal. Examples of such industrial markets include pulp and paper, animal feed, sugar feedstocks (fermentation), and bioethanol. Although we know that white rot fungi are particularly effective in selectively degrading the lignin component of lignin-containing materials, this field is in infancy. The enzymes most commonly purported to bring about lignin degradation – lignin peroxidase, manganese-dependent peroxidase, and laccase – all act as single-electron oxidates and have recently been shown to polymerize, not depolymerize, lignin.

The only report in the literature of a single gene product (enzyme) capable of depolymerizing lignin *in vitro* was contributed by Dr. Simo Sarkanen from the University of Minnesota.

After working with Dr. Sarkanen's lab for about 15 months we were not able to confirm the existence of the LD enzyme or gene. However, we gained considerable experience in growing and inducing white rot fungi during this period. We also established a new lignin characterization capability at NREL, which we intend to use in attracting collaborators to our programs in the NBC.

Proposed Next Steps:

- Apply HPSEC-MALLS-Dawn EOS methodology to the physico-chemical analysis of other lignins, plant cell wall polymers, and synthetic polymers.

- Optimize purification conditions (especially buffers) using RF3 (IEF). More effective methods for obtaining the higher-pI isoenzyme can be investigated.

- Scale up growth and induction of white rot cultures to test MALLS analysis method.

- Develop and extend Bioinformatics approach to identifying new enzymes which depolymerize or modify kraft lignin in the genomes of white rot fungi recently sequenced by the JGI and/or industry.

Project Title: **Rapid Analysis of Soil Organic Matter to Understand Soil Carbon Dynamics and Storage in Relation to Carbon Management**

Principal Investigators: **Kim Magrini and Robert Evans**
Performance period: 10/01 – 09/03
Award: $449,163
Status: Completed

Goals:

- Establish NREL capability for rapid soil organic matter analysis leading to an understanding of the dynamics of the soil carbon cycle and storage for carbon management and sequestration applications.
- Establish NREL capability for rapid soil organic matter analysis leading to an understanding of the dynamics of the soil carbon cycle and storage for carbon management and sequestration applications.
- Develop analytical capabilities for rapid and comprehensive analysis of soil organic matter.
- Develop a metric for soil carbon content. Use the information gained to understand carbon cycling and storage in soil.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - Chronosequence of degraded loblolly pine roots and soils taken 0.5 m and 1 m from the roots has been analyzed. Principal component analysis and PLS modeling allowed to predict the age of the roots from py-MS analysis. Additionally, the root inputs into the soil from the roots as a function of time was observed.

   - Work on modeling SOM content in soils is continued. The ability to distinguish till and no till soils is a significant result. Continued analysis of the original Tionesta forest soils samples from the FS showed that we can distinguish hardwood from softwood soil carbon inputs up to 2 meters from the tree in the 0-10 cm depth increment. Currently work is being done on modeling the other known characteristics of soil samples. This work will define the breadth of applicability of our technique and will become a journal article in the last quarter of FY03.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

   - Magrini, K.A.; Evans, B.; Hoover,C.M. (Forrest Service). “Use of Pyrolysis Molecular Beam Mass Spectrometry (py-MBMS) to Characterize Forest Soil Carbon: Method and Preliminary Results”, *Environ. Pollution*, 1002; 116, p. S255-S268.

   - Hoover, C.M. (FS); Magrini, K.A.; Evans, B. “Use of Pyrolysis Molecular Beam Mass Spectrometry (py-MBMS) to Characterize Forest Soil Carbon: Preliminary Results from an Old-Growth Forest in Northwestern Pennsylvania”, *Environ. Pollution*, 2002 116, p. S269-S275.

   - Hoover, C.M.; Magrini, K.A. “A rapid analysis method for determining soil carbon and nitrogen measurements in forests”, poster presented at the Northeast Agroforestry Conference, Oct. 1-5, 2001, Binghamton, NY.

- Magrini, K.A.; Evans, B.; Hoover, C.M.; Looker, M. "Characterization of soil organic matter with rapid pyrolysis molecular beam mass spectrometry (py-MBMS)", presented at the ACS Division of Fuel Chemistry Session on CO_2 Capture and Sequestration and by the Nuclear Chemistry Division session on Analytical Chemistry in Nuclear Technology at the ACS National Meeting in Orlando, Florida, April, 2002.

- Hoover, C.M.; Magrini, K.A; Birdsey, R. "Soil Carbon in Managed and Unmanaged Forests: First Year Results from a Regional Study", accepted for presentation at the USDA Symposium on Natural Resource Management to Offset Greenhouse Gas Emissions, November 19-21, Raleigh, NC.

- Hoover, C. M., Magrini, K.A., Birdsey, R.; Evans, R.J., "Measuring Soil Carbon in Managed Northern Forests: Preliminary Results from a Regional Study, to be presented at the 2002 Soil Science Society of America Annual Meeting, Indianapolis, IN, November 10-14, 2002.

- Heath, L., Hoover, C.M., Magrini, K.A. "Using Site-specific Measurements for Estimating Regional Forest Floor Carbon Pools", to be presented at the 2002 Soil Science Society of America Annual Meeting, Indianapolis, IN, November 10-14, 2002.

- Magrini, K.A., Hoover, C.M., Evans R.J. "Using Pyrolysis Molecular Beam Mass Spectrometry (py-MBMS) to Characterize Soil Organic Carbon in Northern Forests", accepted for presentation at the USDA Symposium on Natural Resource Management to Offset Greenhouse Gas Emissions, November 19-21, Raleigh, NC.

- Magrini, K., Hoover, C., Evans, R.J.; Davis, M.; Looker, M., "Rapid Assessment of Soil Organic Matter Using Pyrolysis Molecular Beam Mass Spectrometry", Second Annual Conference on Carbon Sequestration: Developing and Validating the Technology Base to Reduce Carbon Intensity", Alexandria, VA, May 5-9, 2003.

- Ludovici, K.H.; Magrini, K.A.; Evans, R.J. "Soil Carbon Inputs from a Chronosequence of Decaying Roots Determined by Pyrolysis Mass Spectrometry", Second Annual Conference on Carbon Sequestration: Developing and Validating the Technology Base to Reduce Carbon Intensity", Alexandria, VA, May 5-9, 2003.

- Attended a meeting sponsored by the Colorado chapter of the Soil and Water Conservation Society's "Carbon As a Potential Commodity" . Denver, CO, December 2002.

- Hoover, C.M.[1], Magrini, K.A.; Evans, R.J. "Influence of tree species on the chemistry of soil organic carbon", presented at the Soil Ecological Society Annual Meeting, Palm Springs, CA, May 11-14, 2003.

- Two proposals submitted to NRI and the Joint Fire Science Agencies on measuring soil carbon changes after controlled burns. Funding declined on both. June 2003.

- Proposal to the Forest Service's Southern Global Change Program to analyze the effects of controlled burns on soil organic matter. Prepared July 2002. No news on funding.

- Ludovici, K.; Sanchez, F.; Hoover, C.M.; Magrini, K.A. USDA Agenda 2020 Proposal: Quantifying Carbon Forms in Tree Roots and Soils: Can Py-MS detect differences in rotation length, soil drainage, and fertility treatments. Submitted June 2003.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

- Mr. Gabe Olchin, an undergraduate science major at CSU was hired to help with sample preparation, analysis, and interpretation of soil data. Gabe continued with us full time during the summer through the SULI program and began data analysis of the USDA soil sample set.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

- *U.S. Forest Service*: Our collaborators at the FS North Eastern Research Station (NERS) have expanded forest soil sampling to include all seven sites throughout the eastern and central portions of the U. S. One goal is determining if py-MBMS can detect differences in soil carbon from varied management practices applied to the sites. We as well are working with CSU (Ron Follett) and USDA NRCS (John Kimble) to assess their well-characterized soil sample set. Also ongoing is a collaboration with the FS Southern Global Change Program to analyze a chronosequence of decayed roots and associated soil samples.

- Boise-Cascade: The results of the April sampling trip provided the basis for a joint submission to OS's RFP described above. Boise-Cascade provided additional samples (root and soil) to us from old growth poplars. This work is confidential. Mark Davis arranged for Dr. John Johnson (Washington State University) to send us his soil samples from the same area we sampled at Boise-Cascade. His samples are fractionated into light and heavy fractions and we will project this MBMS data into the original Boise sample for more complete interpretation. We are working on an article that completes this work.

- University of Tennessee: Dr. Steve Thomas introduced us to Dr. Donald Tyler, expert in agricultural soil management, of the University of Tennessee Institute of Agriculture. We talked with Don in December about a potential sampling trip to their 1800 acres of variable land use forest/farm outside of Memphis. The sites have long-term and ongoing management experiments of wide variety and would provide a broad range of samples to analyze with MBMS. Don is interested in collaborating on such a study and will provide samples using statistical sampling methodologies. One site can provide samples from 40-years of no till agriculture. Sampling is complete and we should be receiving prepped samples in the coming quarter. This collaboration allows us to begin analyzing agricultural samples and assessing the effect of agricultural practices on soil carbon. A desired goal of this work is joint publications with the University of Tennessee. Additionally, Don's group works with the ORNL feedstocks group. We likely will begin analysis of these samples in the 4^{th} quarter of FY03.

Impact/Significance:

- Carbon sequestration in the terrestrial biosphere, more specifically the storage of carbon in plant biomass and soils, offers an attractive option for carbon management.

- Soil organic matter (SOM) comprises an especially large pool of carbon in many ecosystems and there has been increasing emphasis placed on enhancing carbon sequestration in this pool through timely manipulation of agricultural and forest lands. Existing methodologies for measuring the carbon in SOM are time-consuming and expensive which are serious limitations, as they often require extensive replication or order to identify statistically significant differences between or among treatments. In addition, efforts to characterize SOM have also been limited, are time consuming, require destructive sampling, and thus often preclude broad-scale application across a range of sites.

- The researchers are using NREL's expertise in molecular beam mass spectrometry (MBMS) and multivariate statistical analysis to characterize soil organic matter, as well as correlate and complement the results with NREL solid-state NMR and ORNL Raman soil analysis.

- The researches propose to develop rapid and comprehensive analyses of soils that will allow a better understanding of specific scientific issues, and use this technology for measurement and monitoring.

- The fundamental research and development of this analytical capability will centrally position NREL as the lead lab in rapid soil analysis within the National Bioenergy Center and the Forest Service Northern Global Change Program.

Proposed Next Steps:

- Continue analyzing the forest soil sample sets, the resampled Boise-Cascade soils, and the agricultural soils from the University of Tennessee. These sets will provide a look at forest management, poplar management, and agricultural management practices on SOM.

- Prepare several publications the remainder of 2003.

- Present joint papers at the Ecological Society of America's meeting in Tucson in August and at the Soil Science Society of America's annual meeting in Indianapolis in November.

- Submit two joint abstracts to the USDA Symposium on Natural Resource Management to Offset Greenhouse Gas Emissions, Raleigh, November 19-21, 2002.

Project Title:	**Characterization of the CO-oxidation System of a Novel Photosynthetic Bacterium**
Principal Investigator:	**Pin-Ching Maness**
Performance period:	2/01 – 09/04
Award:	$224,000
Status:	In progress

Goals:

- Purify and characterize the CODH enzyme;
- Purify and characterize the CODH-specific cofactor protein;
- Investigate various encapsulation techniques in stabilizing these two proteins once purified;
- Gain insight as to how CO levels regulate and maintain the overall CO shift activities.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

- Biochemical study: During the third quarter of FY02 (April-June), we developed (1) a protocol for the detergent solubilization and purification of CO dehydrogenase (CODH), and (2) a protocol for native gel electrophoresis and its activity stain.

- Physiological study: We determined that CO serves as an inducer, initiating the synthesis of new proteins required in the CO oxidation reaction. We also determined that at least 10% CO is required for maximal induction. This result strongly supports the induction data in that with CO serving as an inducer of the CO oxidation reaction, its constant presence is thereby necessary in order to maintain CO oxidation activity both at a higher rate and for a longer duration.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

3. **Resources**: (facilities, staff, equipment, funding, etc.)

   - Purchased an automated enzyme purification system.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

   - Dr. John Baker of Center for Bioenergy System will perform a differential scanning calorimetry for us once we obtain pure protein.

Impact/Significance:

Proposed Next Steps:

   - We will repeat hydroxylapatite chromatography by eliminating ammonium sulfate prior to loading to determine if this matrix is useful for us. Effort from a separate project has resulted in deciphering the complete gene sequence of CODH from CBS. Based on computer simulation, we have obtained a putative three-dimensional structure of the CODH protein. We will perform genetic engineering to modify CODH gene to encode an engineered CODH protein with a modified surface containing a strepavidin tag. If successful, this will eliminate quite a few steps and achieve protein of higher purity in a shorter time frame.

- During next quarter, we will continue to pursue the purification of CODH by gel chromatography in which proteins can be separated based on their differences in molecular weight. We will also investigate if affinity chromatography can be used to purify CODH protein.

Project Title:	**Functional Genomics of Transposon-Tagged Maize Cell Wall Biogenesis-related Genes**
Principal Investigator:	**Steve Thomas**
Performance period:	05/02 – 05/03
Award:	$507,631
Status:	Completed

Goals:

- Demonstrate the utility of near-infrared (NIR) spectroscopy as a genetic screening tool to identify mutant lines carrying lesions in genes that affect cell wall chemistry in corn.
- Develop field methods for sample collection.
- Develop lab methods for collection of good quality NIR spectra from dried leaf segments.
- Develop field methods for collection of good quality NIR spectra from live leaves.
- Determine whether leaf NIR spectral data can be used to predict stover composition.
- Develop a preliminary calibrated method to determine leaf composition from NIR spectra.
- Attempt to correlate wet spectra with dry spectra.
- Initiate a backcrossing scheme to reduce transposon number in candidate lines.
- Demonstrate a capability in plant biotechnology/genomics.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

    - Developed methods for gathering and preserving analogous tissue samples from large numbers of plants in a field setting over a short period of time.
    - Developed and improved methods for gathering NIR data from dried leaf segments and live leaves.
    - Conducted independent screens of leaf and stover materials and attempted to correlate the results.
    - Used Principal Component Analysis to significantly reduce the number of candidate mutant families under consideration.
    - Developed a preliminary calibrated method to determine the composition of leaf segments from NIR data.
    - Initial crosses were made between candidate mutants and inbred lines to begin the process of eliminating uninformative transposons.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

    Three oral presentations about this work have been made by S. Thomas at various scientific meetings:

    - "Functional Genomics Approach to Maize Cell Wall Biochemistry", by Thomas, S.R.; Vollbrecht, E.W.; Meglen, R. presented at The American Chemical Society Annual Meeting in San Diego, CA, April, 2001.

    - "Near-infrared Spectroscopy as a Genetic Screening Tool for Cell Wall Chemistry", by Thomas, S.R.; Hayward, T.K.; Sluiter, A.D.; Jurich, C.K.; Templeton, D.W.; Roth, C.; Hames, B.R. presented at an international meeting entitled Plant Cell Walls at Lake Arrowhead, CA, May, 2002

3. **Resources:** (facilities, staff, equipment, funding, etc.)

    - Project title: "Identification and characterization of cell wall mutants in maize and arabidopsis using novel spectroscopies".
      Funding: $5.9 million over four years from National Science Foundation (NSF). Funding commenced 10/02.

      This is a multi-institutional grant shared between Purdue University, University of Wisconsin, University of Florida, and University of Connecticut, with Purdue as the lead institution. The purpose of this project is to:

        - Screen comprehensive mutant collections in corn and Arabidopsis using FTIR and NIR spectroscopic methods, and molecular biological methods

        - Identify mutations and genes that affect cell wall chemistry

        - Classify the mutations by metabolic type

        - Determine the biochemical function of affected genes.

      Though funds are not provided by NSF to support NREL staff salaries (NSF rules), Thomas will participate as a Visiting Scientist at Purdue University and the grant will pay the salaries of a series of postdoctoral scientists who will do research at NREL. Limited funds (~$100K/4 years) are also available from the NSF grant to support pyrolysis-MBMS work to be done via an Analytical Services Agreement(s).

4. **Collaborations:** (partnerships, sub-contracts, etc.)

- Drs. Erik Vollbrecht and Rob Martienssen, Cold Spring Harbor Laboratory, Cold Spring Harbor, NY, provided corn seed for mutant and inbred lines. Dr. Vollbrecht also provided advice on corn cultivation, corn genetics and interpretation of results. Our interaction extended throughout the length of the project.

- Dr. Pat Bedinger, Department of Biology, Colorado State University, provided field space and advice on corn genetics for our work in the summer of 2001.

- Dr. Wilfred Vermerris, Department of Agronomy, Purdue University, provided the four brown midrib mutations backcrossed into an A619 inbred background (under Materials Transfer Agreement) for use during the summer of 2002.

- Collaborators on the NSF-funded Plant Cell Wall Project include Drs. Nick Carpita, Wilfred Vermerris, Chris Staiger, Brad Reuhs (Purdue University), Drs. Karen Koch and Don McCarty (University of Florida), Dr. Wolf-Dieter Reiter (University of Connecticut), and Drs. Sara Patterson and Tony Bleecker (University of Wisconsin at Madison). The *ad hoc* advisory committee for this project consists of Drs. Ken Keegstra (Michigan State University), Patrick Schnable (Iowa State University), and Jeff Harper (The Scripps Research Institute, La Jolla, CA).

Impact/Significance:

We have shown that that NIR spectroscopy can be used effectively as a fairly high throughput primary screening tool in plant genetics. The results show that that NIR spectroscopy can be used to identify individual plants with unusual cell wall compositions. The result of this screen is to significantly reduce (i.e., by 2-3 orders of magnitude) the number of candidate lines under consideration. The loading spectra from Principal Component models give hints about the type of molecules in cell walls that have been affected by putative mutations, but these suggestions have not yet been confirmed by independent methods. A separate NIR-based screen of fully mature corn stover (i.e., milled whole plants) has yielded a second set of candidate lines for which the bulk chemical composition of whole plant stover is unusual. The techniques developed in this project can be used to identify lines that carry mutations in genes that are involved in cell wall metabolism. This is a first step towards the cloning and characterization of such genes.

Proposed Next Steps:

Methods, procedures and data analysis strategies developed in this project will be used in a follow-on NSF-funded project (described above). Candidate lines identified in this project may be further characterized under the NSF project.

Project Title: **Pentose Transport and Assay Development**

Principal Investigator: **Min Zhang**
Performance period: 06/03 – 07/05
Award: $356,618
Status: In progress

Goals:

- Establish NREL capability as a leader of sugar transport engineering.
- Establish methodologies to study structure and function relationships of xylose transport proteins.
- Establish rapid and reliable assays for analysis of the kinetics of sugar transport.
- Obtain proof of concept and preliminary results to submit a larger proposal to DOE office of Science program.

Accomplishments:

Laboratory work on this project has not been started yet due to a lack of personnel.

1. **Technical:** (scientific, IP creation, etc.)
    - A review of the relevant literature is ongoing.

2. **Visibility:** (proposals, presentations, publications, conferences, etc)

    - An advertisement for a postdoctoral associate was placed in the June 6th issue of Science and at NREL web site. To date very few applications have been received.
    - Microbial physiologists and geneticists were contacted in order to identify potential postdoctoral candidates.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

Identify or create better transporters that are highly efficient at transporting sugars and expressing them in ethanol producing microbes.

As very little is known about the structure-function relationships of pentose transport proteins, it is difficult to predict if transport activity can be improved by expression of modified transporters in microorganisms.

Proposed Next Steps:

If the location of hydrogen ion binding and transport is conserved among transport proteins, then it may be possible to remove the hydrogen ion requirement from the *E. coli*

Energy Analysis

Project Title: **Expert System for the Modeling of Renewable Energy**

Principal Investigator: **Walter Short**
Performance period: 03/03 – 02/05
Award: $142,000
Status: In progress

Goals:

- Develop a web site with reduced form models for wind and PV that can be used by other modelers to better represent the potential of renewable energy.
- Better represent renewables in others' models, assist with better decisions by policy makers that rely on those models, and enhance international reputation for NREL in this area.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - Outlined the basic web page format and developed a prototype

   - Developed initial wind supply curves that include transmission costs. These are based on the GIS analysis, not the WinDS model runs.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

3. **Resources** (facilities, staff, equipment, funding, etc.)

   - Funding is expected in FY2004 for completion of the PV model, using our WinDS model for specific analyses, and expansion of the WinDS model to include hydrogen. Although not directly related to this DDRD effort, these tasks will improve the models that are the starting point for this DDRD project.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

   In anticipation of this capability, three modeling groups have contacted NREL and begun collaborative activities with us. These include PNNL's Second Generation Model group, Chris Namovicz at the EIA (NEMS wind modeler), and Lorna Greening, a private consultant to DOE and EPA who works on MARKAL.

   - Don Hansen of ANL has also expressed an interest with regard to his AMIGA model.
   - David Evans of RFI for the Haiku model.
   - Juanita Haydel of ICF for the IPM model.

Impact/Significance:

Proposed Next Steps:

- Insert the GIS-based wind supply curves into the web page.
- Conceptualize the initial reduced form that will convey the results of the WinDS model.

Hydrogen Production, Delivery, Storage, Use and Infrastructure

Project Title: **Integrating Steam Pretreatment and Anaerobic Digestion: a Flexible Strategy for Biomass Conversion to CH_4, H_2, and Co-Products**

Principal Investigator: **Stefan Czernik & Pin-Ching Maness**
Performance period: 05/03 – 02/05
Award: $300,000
Status: In progress

Goals:

- Establish NREL capability in the anaerobic digestion area using fermentative organisms to produce H_2 and CH_4 from lignocellulosic biomass.
- Develop and optimize an integrated approach combining both biomass pretreatment and anaerobic digestion technologies to produce both H_2 and CH_4 from lignocellulosic biomass.
- Prove the concept that steam/aqueous pretreatment of biomass results in the enhanced digestibility by thermophilic microorganisms leading to the conversion of the carbohydrate fraction of the biomass into CH_4 and CO_2 with yields that can reach 24 kg of CH_4 per 100 kg of lignocellulosic biomass.
- Investigate whether H_2 could be directly produced by anaerobic digestion via the suppression of the methanogenic functions and enhancement of the activity by the H_2-producing thermophiles.
- Establish optimum conditions for the pretreatment of biomass to produce methane and hydrogen by anaerobic thermophilic fermentation.
- Determine efficiency of producing hydrogen from biomass by direct and indirect fermentation process (through methane).

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

   - Sewage sludge obtained from the Denver Waste Water Treatment Plant was proved to contain a rich mixture of microbes capable of producing hydrogen from glucose fermentation.

   - Heat shock treatment (baked at 105°C for 2 hours, or boiling 15minutes) was proved to be effective in inactivating methanogen from converting hydrogen into methane. This significant finding meets the milestone of “Heat shock for methanogen inactivation” (August 2003).

   - Optimal amounts and frequency of glucose feedings for maximal hydrogen production were determined.

   - It was determined that repeated glucose feeding is necessary to sustain hydrogen production.

- Molar yield of hydrogen per glucose is: 1.9□mol H_2/□mol glucose, which is 50% of the theoretical maximum.

- Thermophilic microbes are present in the sewage sludge which produce hydrogen from glucose at 55°C. No hydrogen oxidation was observed under elevated temperature.
- Preliminary studies indicated that microbes in the sewage sludge are capable of using cellulose directly (provided as Avicel) to support hydrogen production, although for a shorter duration.

- Corn stover samples were impregnated with water to 58% moisture content then treated in the AFUF steam gun at five severity conditions. After the steam treatment, hemicellulose fraction was washed out with water from the remaining solid lignocellulose.

- Both liquids and solids have been analyzed to determine elemental and fractional composition. The results of the analyses will be available shortly.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)
   - A proposal for funding more research in the area of biomass pretreatment/ anaerobic digestion was submitted to the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program.

3. **Resources:** (facilities, staff, equipment, funding, etc):

   - A post-doctoral researcher started working on the project in September 2003. He graduated from the University of Oklahoma where he specialized in biological conversion of synthesis gas to alcohols. In additions to this project, he will be an important asset for Biomass Program linking sugar and syn-gas platforms.

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

Impact/Significance:

- Direct utilization of biomass by microbes is extremely slow and currently available pretreatment technologies often release lignin degradation byproducts that are biocidal to the microbes. NREL applies a thermo-mechanical steam pretreatment of biomass that solubilizes hemicellulose and makes the cellulose microstructure more accessible to anaerobic microorganisms. Both solid and liquid fractions from the pretreatment are then exposed to microbial consortia under anaerobic, thermophilic condition to produce H_2 and CH_4 from carbohydrates while also generating a lignin-derived end product suitable for use as compost or fertilizer.

Proposed Next Steps:

- Use substrates from steam-explosion treatment to support microbial hydrogen production.

- Determine parameters such as substrate loading, optimal temperature, etc., for sustained hydrogen production.

- Enrich and isolate natural organisms from sewage sludge capable of degrading cellulose directly to produce hydrogen.

Project Title: **Supercharged Fuel Cell Power System**

Principal Investigator: **Tony Markel**
Performance period: 03/03 –10/03
Award: $28,300
Status: In progress

Goals:

- Produce simulation results from ADVISOR to quantify the potential for system cost, mass, and volume reductions as a function of the inlet flow compositions and technology used to control the composition for an automotive fuel cell system.
- Secure DOE support for continued systems analysis and development.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.)

    - The literature has been reviewed for the effects of oxygen concentration on fuel cell performance.
    - Preliminary vehicle simulations have begun with the revised model, and those support the initial expectations that the system can provide a fuel economy improvement on aggressive driving profiles, e.g. the US06 drive cycle.

    - A record of invention (NREL IR # 02-30) was filed in August of 2002 to document the concept of oxygen supercharged fuel cell power system.

2. **Visibility:** (proposals, presentations, publications, conferences, etc.)

    - Analysis results have been presented to DOE in mid-September 2003.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

4. **Collaborations**: (partnership, sub-contracts, CRADAs, WFOs, etc.)

Impact / Significance:

- The design of experiments results will help define the general operating characteristics required of an oxygen supercharging device for use with the fuel cell system.

Proposed Next Steps:

- The results will be used to secure project funding by DOE in FY04 to fund further research and development efforts in this area.

- Give a presentation to DOE.

Project Title: **Comparative Study of the Interaction of Fe(II) and Mn(II) with the Manganese-binding Site of the Oxygenic Photosynthetic Apparatus**

Principal Investigator: **Michael Seibert**
Performance period: 11/99 - 11/02
Award: $264,600
Status: Completed

Goals:

Advance scientific knowledge of photosynthesis by helping to define the assembly process and structural organization of the water-oxidizing system in the photosynthetic membranes of algae.

Accomplishments:

1. **Technical:** (scientific, IP creation, etc.):

   - The discovery that Fe(II) can block the function of the high affinity Mn-binding site (the nascent catalytic site associated with the photosynthetic water-splitting apparatus) of photosystem II(PSII).

   - Blocking of this site can restore some the functional characteristics of the donor side of PSII.

   - The blocking effect can be used as a tool to study the function of PSII.

   - Arginine amino acid residues on the donor side of PSII are involved in the binding/activity of the 4Mn/Ca/Cl catalytic site.

   - Arginines participate in the formation of the binding domain for the co-factor chloride in PSII.

2. **Visibility:** (proposals, presentations, publications, conferences, etc)

   - Proposal: "Metal Binding on the Oxidizing Side of Photosystem II," submitted January 2003 to the Office of Science(Energy Biosciences) by Michael Siebert for $100K.

   - Semin, B.K.; Ghirardi, M.L.; Seibert, M. "Blocking of Electron Donation by Mn(II) to $Y_Z^{\cdot}$ Following Incubation of Mn-Depleted Photosystem II Membranes with Fe(II) in the Light," *Biochemistry*. 2002. 41, 55854-5964.

   - Semin, B.K.; Ghirardi, M.L.; Seibert, M. "Iron bound to the High-Affinity Mn-binding site f the oxygen-evolving Complex Shifts the pK of the Component Controlling the Electron Transport via Y_Z.," 2003. paper submitted.

   - Makarova, V.V.; Ghirardi, M.L.; Semin, B.K.; Seibert, M. "Role of Arginine Residues in the Oxygen-Evolving Complex of Photosystem II", 2003. In preparation for publication.

   - Seibert, M. was elected a Fellow of the American Association for the Advancement of Science during the tenure of this project.

3. **Resources:** (facilities, staff, equipment, funding, etc.)

4. **Collaborations:** (partnerships, sub-contracts, CRADAs, WFOs, etc.)

- Boris Semin and his colleagues at Moscow State University, Moscow, Russia. Boris Semin has visited from Moscow State University several times during the DDRD Project. This has led to an extended relationship in which he will return to NREL each Fall to continue collaborating with our lab. He brings capability in the Biophysics of photosynthetic systems and continues to work with us while he is in Moscow.

- Lera Makarova, a post-doc under this project, was hired. At the end of her tenure, she left for a job at Ohio State University, but will continue to collaborate with NREL.

Impact/Significance:

These results represent exciting new information about the donor side of PSII and will provide the tools for increased understanding of the water-splitting apparatus and the processes it catalyzes.

Proposed Next Steps:

Collaboration on this work and on other projects with our Russian colleagues, which this DDRD Project catalyzed, will continue.

Appendix B. Acronyms and Symbols

Al – aluminum

ARI – Amalgamated Research Incorporated

BES – DOE Office of Basic Energy Sciences

CA -- California

CdSe – cadmium selenide

CFD – computational fluid dynamics

CH_4 – methane

CO – Colorado

CO – carbon monoxide

CO_2 – carbon dioxide

CRADA – cooperative research and development agreement

CVD – chemical vapor deposition

DDRD – Director's Discretionary Research and Development

DG – distributed generation

DIME – Dynamic Industrial Materials Exchange

DNA – deoxyribonucleic acid

DOE – Department of Energy

EE – DOE Office of Energy Efficiency and Renewable Energy

EVA – ethylene vinyl acetate

Fe – iron

FL – Florida

FTE – full-time employee

FTIR – Fourier transform infrared

FY – fiscal year

GaAlAs – gallium aluminum arsenide

GaAs – gallium arsenide

GaInAs – gallium indium arsenide

GaInP – gallium indium phosphide

GO – DOE Golden Field Office

H – atomic hydrogen

H_2 – molecular hydrogen

H+ – hydrogen ion

HOMER – Hybrid Optimization Model for Electric Renewables

HWCVD – hot-wire chemical vapor deposition

INEEL – Idaho National Engineering and Environmental Laboratory

InP – indium phosphide

ITO – indium tin oxide

K – thousand

KGA – 2-ketoglutaric acid

LA – Louisiana

LED(s) – light-emitting diode(s)

LEO – lateral Epitaxial overgrowth

Li – lithium

Li+ – lithium ion

M – million

M3EH-PPV – poly[2,5-dimethoxy-1,4-phenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-1,2-ethenylene]

MA – Massachusetts

Mn -- manganese

Mw – molecular weight

MW – megawatt

MWNT – multi-wall nanotubes

NCPV – National Center for Photovoltaics

NH – New Hampshire

NIR – near infrared

NM – New Mexico

NO_x – nitrogen oxides

NREL – National Renewable Energy Laboratory

NSF – National Science Foundation

O – oxygen

OEC – oxygen evolving complex

OIT – DOE Office of Industrial Technologies

ORNL – Oak Ridge National Laboratory

PBI – perylene benzimidazole

PCA – principal component analysis

PCBM – [6,6]-Phenyl C_{61}-butyric acid methyl ester

PI – principal investigator

PPEI – perylene-bis(phenethylimide)

PPyEI – perylene-bis(piridylethylimide)

PSII – photosystem II

PV – photovoltaics

R&D – research and development

RET(s) – renewable energy technology(ies)

Ru – rhuthenium

RuO_2 – rhuthenium oxide

Sb – antimony

Si – silicon

SMB – simulated moving bed

Sn – tin

SnO_2 – tin oxide

SnO_2:Sb – antimony-dope tin oxide

STM – scanning tunneling microscope (or microscopy)

SWNT(s) – single-wall nanotubes(s)

TCO – transparent conducting oxide

TiO_2 – titanium dioxide

TN – Tennessee

TOF – time-of-flight

US or U.S. – United States

UV – ultraviolet

V – volt(s)

Vis – visible

VOC(s) – volatile organic compound(s)

WFO – work for others

WI – Wisconsin

yr – year

Zn – zinc